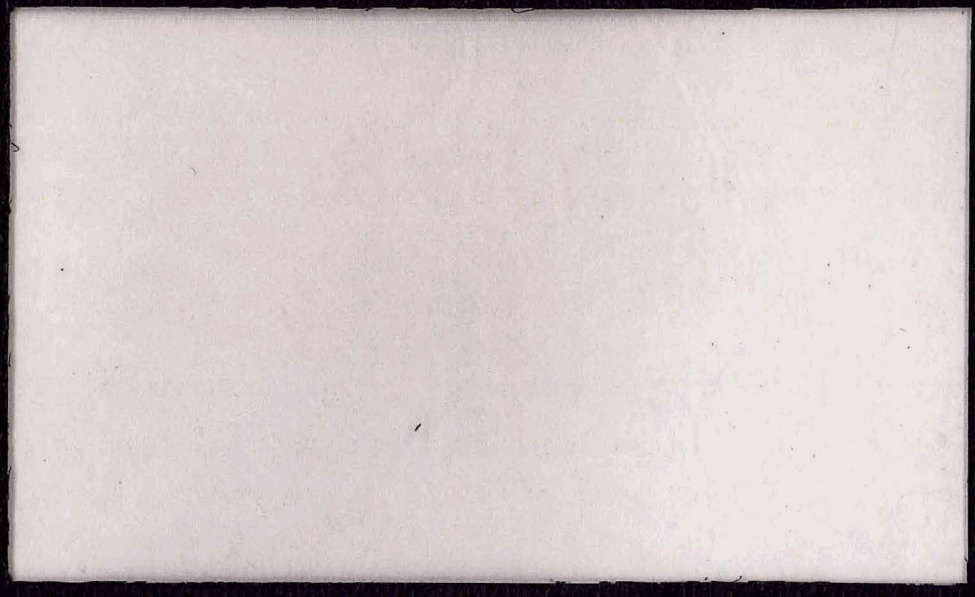

ALLIS-CHALMERS

DISCLAIMER

ACNP-66538

LA CROSSE BOILING WATER REACTOR

RADIO AND WATER CHEMISTRY

MANUAL

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INTRODUCTION

This manual contains the essential material to optimize the LACBWR power plant requirements by inter-relating radiochemistry and a water chemistry program as outlined in this report. The procedures are numbered according to a particular category, such as RC series, radiochemistry methods; WC series, water chemistry methods and the D series dissolution methods. The manual has eight sections which are as follows:

Section I - "Safety"
This section describes the safety needed in the laboratory.

Section II - "Standardization of Carrier Solutions"
This section covers the preparation of carrier solutions and standardization procedures to conform with the carrier requirements of the radiochemical procedures in Section V.

Section III - "Counting Techniques and Data Handling"
This section provides a working knowledge to analyze and report data intelligently.

Section IV - "Water Chemistry Methods"
This section is a collection of water chemistry procedures for determining constituents in reactor steam and water.

Section V - "Radiochemistry Methods"
This section is a collection of radiochemical procedures for determining the activity of selected radionuclides.

INTRODUCTION (Cont'd)

Section VI - "Dissolution Methods"

This section is a collection of dissolution procedures for quantitative removal of sorbed activity from ion exchange resin and dissolution of insoluble corrosion products.

Section VII - "Schedule for Radio and Water Chemistry Analyses"

This section lists the analyses needed during the operation of the reactor.

Section VIII - "Appendix"

SECTION I

SAFETY

This section will describe in detail the safety needed in the laboratory. Principles of safe laboratory practices should be exercised at all times.

The following summarizes the safe laboratory practices:

a. Personnel protective equipment such as eye protection, face shields, and gloves shall be used when necessary.

b. Safety glasses must be worn in the laboratory. Full face shields may be necessary for certain operations.

c. Rubber gloves shall be used when pouring acids such as fuming nitric acid and hydrofluoric acid or when handling radioactive material. Surgeon's gloves may be used when manual dexterity is required.

d. An acid and alkaline resistant laboratory coat shall be used in the laboratory at all times to protect the clothes and body from corrosive chemicals and radioactive contamination.

e. Smoking, eating and drinking are forbidden in the laboratory.

I. SAFETY (Cont'd)

f. Avoid skin contact and inhalation or ingestion of all chemicals.

g. Broken glassware shall be disposed of in a separate container.

h. The fume hood should be used when handling volatile or flammable chemicals.

i. Do not pick up small splinters of broken glass with the hands. Use a whisk broom and dust pan. Very small pieces may be picked up with a large piece of wet cotton or sticky paper.

j. Contaminated waste shall be segregated from clean debris.

k. In dilution of strong acids, always add acid to the water slowly over a sink or vessel to contain any breakage or spillage. Acid should first be transferred to a small beaker or reagent bottle rather than attempting to transfer directly from large stock bottles of reagents

l. Flammable liquids and corrosive, noxious, or vapor-producing chemicals shall not be poured in the sink but shall be stored in the containers provided. Acids and alkalis may be flushed down the sink with copious amounts of water for dilution, or else should be neutralized before disposal.

I. SAFETY (Cont'd)

m. All reagent bottles and other containers of chemicals shall be clearly labeled. These shall not be filled to more than three-quarters of their capacity to allow for expansion.

n. Never mix organic chemicals and acids except as specifically detailed in procedures.

o. Never pipette by mouth. Use rubber bulb or equivalent to apply the suction.

p. All precautions used in handling corrosive and toxic chemicals shall also be observed with radioactive sampler.

q. Mercury vapor is poisonous. Use trays to contain spills when working with mercury, and clean up all spillage.

r. Before analyzing primary coolant, the radiation levels shall be monitored to ascertain what precautions must be taken.

s. Evaporations involving primary coolant must be performed in the fume hood.

t. Hands and clothing shall be monitored for contamination before leaving the laboratory.

The following are the safe laboratory technique practices:

I. SAFETY

Evaporation

Evaporation in beakers and flasks should be made on a hot plate. To prevent "bumping", a few glass beads may be added. Infra-red lamps may be used to evaporate small liquid samples in planchets. Solutions in centrifuge cones, can be evaporated by placing a flame directly below the liquid level in the cone. The cone should be held with tongs, not the fingers, and given a continous swirling motion to avoid over-heating the liquid in any one place. This technique takes practice in order to avoid the loss of liquid. Evaporate organic solvents in a water bath under a fume hood. Solutions needed to be heated can be placed in a beaker half filled with water and placed on a hot plate.

Centrifuge Practice

When using the centrifuge be sure that the cone containing the sample is counterbalanced by another tube containing the same level of liquid. The centrifuge should be thick-walled glass or plastic to allow the use of the highest speed on the centrifuge. Allow the centrifuge to come to a stop by itself, unless it has a brake attachment which can be used with caution. Otherwise, the precipitate may become dislodged. If

I. SAFETY

Centrifuge Practice (Cont'd)

the precipitate become difficult to come down after centrifuging for two minutes, the addition of a few drops of a wetting agent will remedy this problem.

Filtration

The final precipitate from the radiochemical procedures is usually suction filtered. The stainless steel filtering apparatus is placed in a 500 ml sidearm flask through a one-hole rubber stopper. The flask is connected to an explosion-proof vacuum pump by means of a vacuum hose and an intermediate empty filtering flask used as a liquid trap. The filter paper should be centered on the filter support. A few drops of water should be poured onto the filter to wet the filter. After this operation is completed turn on the pump and pour the precipitate onto the filter. After the washing of the precipitate with ethyl alcohol and removing moisture with ether, the pump should remain on for around 30 seconds. The top of the filtering apparatus is then removed with the vacuum pump on. The pump is turned off and the filter paper is removed with blunt-point forceps (blunt type should be used to prevent putting holes in the filter paper).

SECTION II

STANDARDIZATION OF CARRIER SOLUTIONS

A. SUMMARY OF METHODS

The losses of a radioelement through the radiochemical procedure is determined by measuring the fractional recovery of the carrier element used. This requires the addition of a known amount of carrier element at the beginning of the analysis. To accomplish this, carrier solutions are prepared, standardized and accurately measured volumes of the solutions are used.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Glass Fiber Filter - 1 inch diameter x 0.01 inches thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to $\pm$ 0.0001 gm during filtration and drying.

3. Filter Holder - The filter holder must hold the 1 inch filters rigidly in place during filtration.

NOTE: Care should be taken to clean the holder thoroughly between filtrations to prevent cross-contamination.

4. Desiccator - The desiccator must hold four 1 inch diameter filters similar to Fisher No. 8-615.

B. APPARATUS (Cont'd)

5. Oven - Oven should be gravity convection type and be able to supply uniform heat at 110° C to a ± 0.5° C. (Fisher No. 13-244-1 or equivalent).

6. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

7. Muffle Furnace - To be able to hold four crucibles and also designed for continuous operation at temperatures up to 900° C (1650° F). (Fisher No. 10-552 or equivalent).

8. Refrigerator - Small laboratory type designed to be explosion proof.

9. Infra-Red Lamp - The infra-red lamp should be designed to adjust at various heights for evaporating solutions and drying precipitates. (Fisher No. 11-504-5V4 or equivalent).

10. Centrifuge - A clinical centrifuge shall be used. The head should accommodate 50 ml centrifuge tubes.

C. REAGENTS AND MATERIALS

1. Purity of Reagents - Reagent grade chemicals shall be used to prepare carriers. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

STANDARDIZATION OF CARRIER SOLUTIONS

C. REAGENTS AND MATERIALS

2. Purity of Water - All water used in preparing the carriers and in standardization of these carriers shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D 1193).

3. Ethyl Alcohol - Either CP ethyl alcohol or denatured ethyl alcohol (denatured according to formula No. 30, Regulations No. 3 and its appendix, U.S. Bureau of Internal Revenue) shall be used for standardization of the carriers.

4. Cesium Chloride - Cesium chloride reagent No. C-24, purified, which can be obtained from Fisher Chemical Company.

5. Chloroplatinic Acid Reagent - Dissolve 7.3 grams of hydrated chloroplatinic acid ($H_2 PtCl_6 \cdot 6H_2O$) in 100 ml of water.

6. 6M Acetic Acid - Measure 40 ml concentrated acetic acid and dilute to 100 ml with water.

7. 6N Hydrochloric Acid - Measure 498 ml of 12.1 N hydrochloric acid (concentrated) and dilute to 1-liter with water.

8. 1N Hydrochloric Acid - Measure 83.0 ml of 12.1 Hydrochloric acid (concentrated) and dilute to 1-liter with water.

9. 2N Hydrochloric Acid - Measure 166 ml of 12.1N hydrochloric acid (concentrated) and dilute to 1-liter with water.

STANDARDIZATION OF CARRIER SOLUTIONS

C. REAGENTS AND MATERIALS

10. 6N Nitric Acid - Measure 384 ml of 15.7N Nitric acid (concentrated) and dilute to 1-liter with water.

11. 4N Nitric Acid - Measure 256 ml of 15.7N Nitric acid (concentrated) and dilute to 1-liter with water.

12. 3M Ammonium Acetate - Dissolve 230 grams of Ammonium Acetate ($NH_4C_2H_3O_2$) in water and dilute to 1-liter with water.

13. Cupferron Reagent - Dissolve 6 grams of the ammonium salt of nitroso-phenyl-hydroxylamine (cupferron) in 100 ml of water.

NOTE: Reagent good for one week only and must be kept cool and stored in the dark.

14. 1.5M Sodium Chromate - Dissolve 243 grams of sodium chromate (Na_2CrO_4) and dilute to 1-liter with water.

15. 0.1M Palladium Chloride - Dissolve 21.4 grams of palladium chloride ($Pd\ Cl_2 \cdot 2H_2O$) and dilute to 1-liter with water.

16. 1.5N Sulfuric Acid - Measure 42 ml of 36.0 N Sulfuric acid (concentrated) and diluted to 1-liter with water.

17. 14.8N Ammonium Hydioxide - Concentrated ammonium hydioxide (NH_4OH).

STANDARDIZATION OF CARRIER SOLUTIONS

C. REAGENTS AND MATERIALS

18. 15.7N Nitric Acid - Concentrated Nitric Acid (HNO_3).

19. 12.1N Hydrochloric Acid - Concentrated Hydrochloric Acid (HCl).

20. (1-3) Hydrochloric Acid solution - Measure 100 ml of concentrated hydrochloric acid (12.1N)(HCl) and dilute with 300 ml water.

21. The following additional chemicals are needed:

a. Saturated Ammonium Oxalate $(NH_4)_2\ C_2O_4$ Solution
b. Hydrogen Sulfide (H_2S) gas
c. Saturated Sodium Bromate $NaBrO_3$
d. Saturated Oxalic Acid Solution
e. Saturated Barium Nitrate Solution

22. The following chemicals will be needed to prepare carriers:

a. Barium Nitrate $Ba(NO_3)2$
b. Cerium Nitrate $Ce(NO_3)3 \cdot 6H_2O$
c. Cobalt Nitrate $Co(NO_3)2 \cdot 6H_2O$
d. Potassium Iodide KI
e. Iron Chloride $FeCl_3 \cdot 6H_2O$
f. Potassium Chloride KCl
g. Rubidium Chloride RbCl
h. Strontium Nitrate $Sr(NO_3)2 \cdot 4H_2O$
i. Yttrium Nitrate $Y(NO_3)3 \cdot 6H_2O$
j. Zirconyl Nitrate $Zro(NO_3) \cdot 2H_2O$
k. Manganese Dioxide MNO_2
l. Lanthanium Nitrate $(La_2\ (NO_3)_3 \cdot 6H_2O)$
m. Potassium Dichromate $(K_2Cr_2O_7)$
n. Sodium Fluoride (NaF)
O. Sodium Tungstate $(Na_2WO_4 \cdot 2H_2O)$
p. Pure Nickel Metal Powder
q. Pure Copper Metal
r. Sodium Chloride (NaCl)
s. Ammonium chloride (HN_4Cl)

AMMONIUM CARRIER

(10 mg/ml)

1. Dissolve 3 grams ammonium chloride (NH_4Cl) in 100 ml of water.

2. Pipet accurately four 2 ml portions of the carrier solution into four separate 50 ml centrifuge tubes.

3. Dilute to 5 ml with 6N hydrochloric acid (HCl).

4. Add 1 ml of 5 percent chloroplatinic acid (H_2PtCl_6) and 5 ml of ethyl alcohol.

5. Place centrifuge tubes in an ice bath for 5-10 minutes.

6. Filter with suction the precipitate onto a weighed glass fiber filter holder.
NOTE: The precipitate appearance will be a yellow-orange color precipitate.

7. Rinse the centrifuge tube with ethyl alcohol and pour the rinsings through the filter.

8. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

9. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

10. Subtract the tare weight of the filter to obtain the weight of the precipitate.

11. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5%.

CALCULATIONS

$$NH_4 \text{ (mg/ml)} = \frac{\text{mg(ppt)}(NH_4)_2PtCl_6(0.04063)}{\text{ml (aliquote)}}$$

BARIUM CARRIER

(10 mg/ml)

1. Dissolve 19.0 grams of Barium Nitrate ($Ba(NO_3)_2$ in approximately 300 ml of water.

2. Dilute to 1-liter and shake for 1 or 2 minutes.

3. Pipet accurately four 5.0 ml portions of the carrier solution into four separate 250 ml beakers.

4. Dilute to approximately 100 ml.

5. Add 5 ml of 6M acetic acid and 10 ml of 3M ammonium acetate.

6. Place beakers on a hot plate and bring to a boil.

7. Add 5 ml of 1.5M sodium chromate (Na_2CrO_4) dropwise while stirring. Boil for 1 or 2 minutes with stirring.

8. Filter with suction the precipitate onto a weighed flass fiber filter placed in the filter holder.

9. Rinse the beaker with ethyl alcohol and pour the rinsings through the filter.

10. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

11. Place the filter containing the precipitate in an oven and dry at 110° C for 30 minutes. Cool in a desiccator for 2 minutes

BARIUM CARRIER (10 mg/ml) (Cont'd)

12. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

13. Subtract the tare weight of the filter to obtain the weight of the precipitate.

14. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5%.

CALCULATIONS

$$Ba(mg/ml) = \frac{(mg(ppt)BaCrO_4)\ (0.5421)}{ml\ (aliquote)}$$

CERIUM CARRIER

(10 mg/ml)

1. Dissolve 31.0 grams of cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) in 200 ml of water.

2. Dilute to 1-liter and shake for 1 or 2 minutes.

3. Pipet accurately four 5.0 ml portions of the carrier solution into four 100 ml beakers.

4. Dilute to approximately 20 ml with water.

5. Warm on a hot water bath and about 50 ml of saturated ammonium oxalate ($(NH_4)_2C_2O_4$) solution.

6. Cool in an ice bath for approximately 15 minutes and filter with a filter funnel using a 11 cm Whatman No. 42 filter paper.

7. Transfer the precipitate to a tared porcelain crucible and dry under a heat lamp.

8. Cover and ignite for 10 minutes in a muffle furnace at 800° C.

9. Remove the cover and continue the ignition for 30 minutes.

10. Cool and weigh the crucible and precipitate (CeO_2) on an analytical balance to the nearest 0.1 mg.

11. Place the crucible containing the precipitate in an oven and dry at 110° C for 20 minutes.

CERIUM CARRIER (10 mg/ml) (Cont'd)

12. Cool for 20 minutes in a desiccator and reweigh.

13. Repeat steps 11 and 12 until constant weight is obtained.

14. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5%.

CALCULATIONS

$$Ce(mg/ml) = \frac{(mg(ppt)CeO_2)\ (0.8141)}{ml\ (aliquote)}$$

CESIUM CARRIER

(10 mg/ml)

1. Dissolve 12.5 grams of cesium chloride in water and dilute to 1-liter with water.

2. Pipet accurately four 5.0 ml portions of the carrier solution into a 50 ml centrifuge tube.

3. Adjust the volume to 10 ml in 6N hydrochloric Acid (HCl).

4. Add 4 ml of chloroplatinic acid.

5. Stir 1 or 2 minutes and cool in a regrigerator for 10 minutes.

6. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

7. Rinse the centrifuge tube with ethyl alcohol and pour the rinsings through the filter.

8. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

9. Place the filter containing the precipitate in an oven and dry at 110° C for 30 minutes. Cool in a desiccator for 20 minutes.

10. Weigh the filter and precipitate on an analytical balance.

CESIUM CARRIER (10 mg/ml) (Cont'd)

11. Subtract the tare weight of the filter to obtain the weight of the precipitate.

12. Repeat Steps 9, 10 and 11 until constant weight is obtained.

13. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5%.

CALCULATIONS

$$\text{Cs (mg/ml)} = \frac{(\text{mg(ppt) } Cs_2PtCl_6)\ (0.3945)}{\text{ml (aliquote)}}$$

CHROMIUM CARRIER

1. Dissolve 28 grams of potassium dichromate ($K_2Cr_2O_7$) in 200 ml of water.

2. Dilute to 1-liter with water and shake for 1 or 2 minutes.

3. Pipet accurately four 2.0 ml portions of the carrier solution into four separate 50 ml centrifuge tubes.

4. Add 1 ml concentrated ammonium hydroxide (NH_4OH) and 15 ml of water.

5. Add 3 ml of saturated barium nitrate ($Ba(NO_3)2$) solution to precipitate ($BaCrO_4$).

6. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

7. Rinse the 50 ml centrifuge with ethyl alcohol and pour the rinsings through the filter.

8. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

9. Place the filter containing the precipitate in an oven and dry at 110° C for 10 to 15 minutes. Cool in a desiccator for 10 to 15 minutes.

10. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

CHROMIUM CARRIER (Cont'd)

11. Subtract the tare weight of the filter to obtain the weight of the precipitate.

12. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5%.

CALCULATIONS

$$Cr\ (mg/ml) = \frac{(mg(ppt)BaCrO_4)(0.2053)}{(ml(aliquote)}$$

COBALT CARRIER

(10 mg/ml)

1. Dissolve 49.3 grams of Cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ in 200 ml of water.

2. Add 1 ml concentrated Nitric Acid (NHO_3) and dilute to 1-liter with water.

3. Pipet accurately four 5.0 ml portions of the carrier solution into four separate 50 ml centrifuge cover.

4. Dilute to approximately 15 ml with water.

5. Add 2 ml of concentrated ammonium hydroxide (NH_4OH) and carefully saturate the solution with hydrogen sulfide(H_2S) gas.

6. Filter the cobalt monosulfide (CoS) onto a Whatman No. 42 filter paper and wash with 5 ml of ammonia water.

7. Transfer the paper and precipitate to a tared porcelain crucible.

8. Dry under a heat lamp, cover with a porcelain cover and ignite for approximately 10 minutes at 700° C.

9. Remove the cover and continue the ignition for 30 minutes.

COBALT CARRIER (Cont'd)
(10 mg/ml)

10. Cool and weigh the crucible and precipitate (Co_2O_3) on an analytical balance to the nearest 0.1 mg.

11. Place the crucible containing the precipitate in an oven and dry at 110° C for 20 minutes.

12. Cool for 20 minutes in a desiccator and reweigh.

13. Repeat steps 11 and 12 until constant weight is obtained.

14. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5%.

CALCULATIONS

$$Co\ (mg/ml) = \frac{mg(ppt)\ (Co_2O_3)\ (0.7106)}{ml\ (aliquote)}$$

COPPER CARRIER

(10 mg/ml)

1. Dissolve 1.00 gm (pure) copper metal in 25 ml concentrated nitric acid.

2. Dilute to 100 ml with water and shake for 1 or 2 minutes.

NOTE: If the copper metal is weighed on an analytical balance to the nearest 0.1 mg, standardization will not be necessary.

FLUORIDE CARRIER

(10 mg/ml)

1. Dissolve 1.8 gm of sodium fluoride (NaF) in 100 ml of water in a volumetric flask.

2. Shake for 1 or 2 minutes.

3. Pipet accurately four 2.0 ml portions of the fluoride carrier solution into four separate 50 ml centrifuge tubes.

4. Add 20 ml of Lanthanium carrier.

5. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

NOTE: The precipitate appearance will be a white gelatinous precipitate.

6. Rinse the centrifuge tube with ethyl alcohol and pour the rinsings through the filter.

7. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

8. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

9. Subtract the tare weight of the filter to obtain the weight of the precipitate.

10. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5%.

FLUORIDE CARRIER (Cont'd)
(10 mg/ml)

CALCULATIONS

$$F\ (mg/ml) = \frac{(mg(ppt)NaF)(0.1455)}{ml\ (aliquote)}$$

IODINE CARRIER

(10 mg/ml)

1. Dissolve 13.1 grams of potassium iodide (KI) in 200 ml of water.

2. Dilute to 1-liter with water and shake for 1 or 2 minutes.

3. Pipet accurately four 5.0 ml portions of the carrier solution into four separate 100 ml beakers.

4. Acidify with 1 ml concentrated nitric acid (HNO_3).

5. Add about 2 ml 0.1M palladium chloride ($PdCl_2$) to precipitate all the I^-.

6. Digest the precipitate on a hot plate for 10 minutes.

7. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

8. Rinse the beaker with ethyl alcohol and pour the rinsings through the filter.

9. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

10. Place the filter containing the precipitate in an oven and dry at 110° C for 30 minutes. Cool in a desiccator for 20 minutes.

IODINE CARRIER (Cont'd)
(10 mg/ml)

11. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

12. Subtract the tare weight of the filter to obtain the weight of the precipitate.

13. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5%.

CALCULATIONS

$$I\ (mg/ml) = \frac{mg(ppt)\ PdI_2\ (.3378)}{ml\ (aliquote)}$$

IRON CARRIER

(10 mg/ml)

1. Dissolve 48.4 grams of iron chloride $FeCl_3 \cdot 6H_2O$ in 1N hydrochloric acid (HCl).

2. Dilute to 1-liter with 1N hydrochloric acid (HCl) and shake for 1 or 2 minutes.

3. Pipet accurately four 5.0 ml portions of the carrier solution into four separate tared porcelain crucibles.

4. Add concentrated ammonium hydroxide dropwise to precipitate iron hydroxide ($Fe(OH)_3$).

5. Evaporate to dryness under an infra-red lamp.

6. Ignite in a muffle furnace at 700° C for 15 minutes.

7. Cool and weigh the crucible and precipitate (Fe_2O_3) on an analytical balance to the nearest 0.1 mg.

8. Place the crucible containing the precipitate in an oven and dry at 110° C for 20 minutes.

9. Cool for 20 minutes in a desiccator and reweigh.

10. Repeat steps 8 and 9 until constant weight is obtained.

11. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5%.

IRON CARRIER (Cont'd)
(10 mg/ml)

CALCULATIONS

$$Fe(mg/ml) = \frac{(mg(ppt)\ Fe_2O_3)(0.6994)}{ml\ (aliquote)}$$

LANTHANUM CARRIER

(10 mg/ml)

1. Dissolve 15.6 grams lanthanum nitrate ($La_2(NO_3)_3 \cdot 6H_2O$) in 200 ml of water.

2. Dilute to 1-liter with water and shake for 1 or 2 minutes.

3. Pipet accurately four 5.0 ml portions of the carrier solution into four separate 50 ml centrifuge tubes.

4. Add 15 ml of water and place in a beaker half filled with water and heat on a hot plate to boiling.

5. While heating on the hot plate and stirring, add 15 ml of saturated oxalic acid.

6. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

7. Rinse the centrifuge tube with ethyl alcohol and pour the rinsings through the filter.

8. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

9. Place the filter containing the precipitate in an oven and dry at 110° C for 10-15 minutes. Cool in a desiccator for 15 minutes.

10. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

LANTHANUM CARRIER (Cont'd)
(10 mg/ml)

11. Subtract the tare weight of the filter to obtain the weight of the precipitate.

12. Four standardizationsof the carrier solution should be performed. The spread in results should be less than 0.5%.

CALCULATIONS

$$\text{La (mg/ml)} = \frac{\text{mg(ppt)}(La_2(C_2O_4)_3 \cdot 9H_2O)(0.3949)}{\text{ml (aliquote)}}$$

MANGANESE CARRIER

(10 mg/ml)

1. Dissolve 16 grams of Manganese dioxide in 50 ml of concentrated hydrochloric acid (HCl)(12.1N).

NOTE: Heating may be necessary to dissolve.

2. Dilute to 1-liter with (1-3) hydrochloric acid solution (HCl) and shake for 1 or 2 minutes.

3. Pipet accurately four 5.0 ml portions of the carrier solution into four separate 50 ml centrifuge tubes.

4. Add 10 ml concentrated nitric acid (HNO_3) (15.7N) to each centrifuge tube.

5. Add 2 ml saturated sodium bromate ($NaBrO_3$) solution and boil for three minutes by placing the centrifuge tubes into a beaker half filled with water and place on a hotplate.

6. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

7. Rinse the centrifuge tube with ethyl alcohol and pour the rinsings through the filter.

8. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

9. Place the filter containing the precipitate in an oven and dry at 110° C for 10 to 20 minutes. Cool in a desiccator for 10 to 20 minutes.

MANGANESE CARRIER (Cont'd)
(10 mg/ml)

10. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

11. Subtract the tare weight of the filter to obtain the weight of the precipitate.

12. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5%.

CALCULATIONS

$$Mn(mg/ml) = \frac{(mg(ppt)\ MnO_2)(0.6320)}{ml\ (aliquote)}$$

NICKEL CARRIER

(10 mg/ml)

1. Dissolve 1.00 gram (pure) nickel metal powder in 25 ml concentrated nitric acid.

2. Dilute to 100 ml with water and shake for 1 or 2 minutes.

NOTE: If the nickel metal is weighed on an analytical balance to the nearest 0.1 mg, standardization will not be necessary.

POTASSIUM CARRIER

(10 mg/ml)

1. Dry approximately 19 grams of primary standard potassium chloride (KCl) salt at 110° C for 1 hour.

2. Store the dried salt in a glass-stoppered weighing bottle inside a desiccator.

3. Weigh the dried salt on an analytical balance to the nearest 0.1 mg.

4. Transfer the weighed salt to a 1-liter volumetric flask and fill with water to the calibrated line.

5. Mix thoroughly for 5 or 10 minutes.

CALCULATIONS

Calculate the concentration as follows:

$$K(mg/ml) = \frac{(mgKCl)(0.5244)}{(1000\ ml)}$$

RUBIDIUM CARRIER

(10 mg/ml)

1. Dissolve 14.2 grams of rubidium chloride (RbCl) in 500 ml of water.

2. Filter off any undissolved material and dilute the filtrate to 1-liter.

3. Pipet accurately four 5.0 ml portions of the carrier solution into four separate 50 ml centrifuge tubes.

4. Adjust the volume to 10 ml with 6N hydrochloric acid (HCl).

5. Add 4 ml of chloroplatinic acid.

6. Stir for 1 or 2 minutes and let stand for ten minutes at 20° C.

7. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

8. Wash the precipitate three times with 5 ml portions of 6N hydrochloric acid (HCl).

9. Wash the precipitate with approximately 5 ml ethyl alcohol and 5 ml of diethyl ether.

10. Place the filter containing the precipitate in an oven and dry at 110° C for 20 minutes. Cool in a desiccator for 20 minutes.

RUBIDIUM CARRIER (Cont'd)
(10 mg/ml)

11. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

12. Subtract the tare weight of the filter to obtain the weight of the precipitate.

13. Repeat Steps 10, 11 and 12 until constant weight is obtained.

14. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5%.

CALCULATIONS

$$\text{Rb (mg/ml)} = \frac{(\text{mg(ppt) } Rb_2PtCl_6)(0.2903)}{\text{ml (aliquote)}}$$

SODIUM CARRIER

(10 mg/ml)

1. Dissolve 2.5420 grams of sodium chloride (NaCl) in water.

NOTE: Sodium chloride crystals should be dried in an oven at 110° C for 1 hour. Cool in a desiccator before weighing on an analytical balance.

2. Dilute to 100 ml with water and shake for 1 or 2 minutes.

NOTE: This need not be standardized if weighed accurately.

STRONTIUM CARRIER

(10 mg/ml)

1. Dissolve 32.4 grams of strontium nitrate ($Sr(NO_3)_2 \cdot 4H_2O$ in water.

2. Dilute to 1-liter with water and shake for 1 or 2 minutes.

3. Pipet accurately four 5.0 ml portions of the carrier solution into four tared porcelain crucibles.

4. Add 500 (0.5 ml) of 1.5N sulfuric acid (H_2SO_4) solution.

5. With caution, carefully stir the mixture with a thin glass stirring rod.

6. Wash the stirring rod with a minimum quantity of water, while collecting the washings in the crucible.

7. Evaporate to dryness under an infra-red heat lamp.

8. Ignite the crucibles in a muffle furnace at 500° C for 15 minutes.

9. Cool and weigh the crucibles and precipitates on an analytical balance to the nearest 0.1 mg.

10. Place the crucible containing the precipitate in an oven and dry at 110° C for 20 minutes.

11. Cool for 20 minutes in a desiccator and reweigh.

STRONTIUM CARRIER (Cont'd)
(10 mg/ml)

12. Repeat steps 10 and 11 until constant weight is obtained.

13. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5%.

CALCULATIONS

$$Sr(mg/ml) = \frac{(mg(ppt)SrSo_4)(0.4770)}{ml\ (aliquote)}$$

TUNGSTEN CARRIER

(10 mg/ml)

1. Dissolve 1.8 grams sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) in water.

2. Dilute to 1-liter with water and shake for 1 or 2 minutes.

3. Pipet accurately four 5.0 ml portions of the carrier solution into four separate 50 ml centrifige tubes.

4. Add 10 ml concentrated nitric acid and place in a beaker half filled with water and heat on a hot plate. Boil for 10 minutes.

5. Filter with suction the precipitate onto an ashless filter paper.

6. Place the filter paper in a tared 40 ml porcelain crucible and dry under a heat lamp.

7. Cover and ignite for 10 minutes in a muffle furnace at 800° C.

8. Remove the cover and continue the ignition for 30 minutes.

9. Cool and weigh the crucible and precipitate (WO_3) on an analytical balance to the nearest 0.1 mg.

10. Place the crucible containing the precipitate in an oven and dry at 110° C for 20 minutes.

TUNGSTEN CARRIER (Cont'd)
(10 mg/ml

11. Cool for 10-15 minutes in a desiccator and reweigh.

12. Repeat steps 10 and 11 until constant weight is obtained.

13. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5%.

CALCULATIONS

$$W\ (mg/ml) = \frac{(mg(ppt)WO_3)(0.7930)}{ml\ (aliquote)}$$

YTTRIUM CARRIER

(10 mg/ml)

1. Dissolve 43 grams of yttrium nitrate $Y(NO_3)_3 \cdot 6H_2O$ in 500 ml of water.

2. Add 5 ml of 6N nitric acid (HNO_3).

3. Dilute to 1-liter and shake for 1 or 2 minutes.

4. Pipet accurately four 5.0 ml portions of the carrier solution into four separate 50 ml centrifuge tubes.

5. Add 10 ml of water and heat to boiling.

6. While stirring, add 20 ml of saturated ammonium oxalate $(NH_4)_2\ C_2O_4$.

7. Heat for ten minutes on a hot water bath and then cool in an ice bath for 10 minutes.

8. Centrifuge the yttrium oxalate $Y_2(C_2O_4)_3$ and decant the supernatant.

9. Slurry the precipitate in 10 ml of water and filter through a Whatman No. 40 filter paper.

10. Wash the precipitate with three 10 ml portions of water.

11. Transfer the precipitate to a tared porcelain crucible and dry under a heat lamp.

YTTRIUM CARRIER (Cont'd)
(10 mg/ml)

12. Cover and ignite for 10 minutes in a muffle furnace at 800° C.

13. Remove the cover and continue the ignition for 1 hour.

14. Cool and weigh the crucible and precipitate (Y_2O_3) on an analytical balance to the nearest 0.1 mg.

15. Place the crucible containing the precipitate in an oven and dry at 110° C for 20 minutes.

16. Cool for 20 minutes in a desiccator and reweigh.

17. Repeat steps 15 and 16 until constant weight is obtained.

18. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5%.

CALCULATIONS

$$Y\ (mg/ml) = \frac{(mg(ppt)\ Y_2O_3\ (0.7875)}{ml\ (aliquote)}$$

ZIRCONIUM CARRIER

(10 mg/ml)

1. Dissolve 30 grams of zirconyl nitrate ($ZrO(NO_3)_2 \cdot 2H_2O$ in approximately 300 ml of water. (Add sufficient nitric acid (HNO_3) to make the solution 4N in nitric acid (HNO_3).)

2. Filter and make the filtrate up to a volume of 1-liter with 4N nitric acid (HNO_3). (Shake the solution for 1 or 2 minutes).

3. Pipet accurately four 5.0 ml portions of the carrier solution into four separate 50 ml centrifuge tubes.

4. Make the solution 2N hydrochloric acid (HCl) and cool in an ice bath.

5. Add approximately 2 ml of 6% cupferron reagent and filter with a filter funnel using Whatman No. 42 filter paper.

6. Wash the precipitate with 1N hydrochloric acid (HCl) containing a little cupferron.

NOTE: Keep all solutions and zirconium derivative of cupferron cold.

7. Transfer the precipitate to a tared porcelain crucible and dry under a heat lamp.

8. Cover and ignite for 10 minutes in a muffle furnace at 700° C.

ZIRCONIUM CARRIER (Cont'd)
(10 mg/ml)

9. Remove the cover and continue the ignition for 1 hour.

10. Cool and weigh the crucible and precipitate (ZrO_2) on an analytical balance to the nearest 0.1 mg.

11. Place the crucible containing the precipitate in an oven and dry at 110° C for 20 minutes.

12. Cool for 20 minutes in a desiccator and reweigh.

13. Repeat steps 11 and 12 until constant weight is obtained.

14. Four standardizations of the carrier solution should be performed. The spread in results should be less than 0.5%.

CALCULATIONS

$$Zr\ (mg/ml) = \frac{(mg(ppt)ZrO_2)(0.7402)}{ml\ (aliquote)}$$

SECTION III

COUNTING TECHNIQUES AND DATA HANDLING

This section will provide a working knowledge to analyze and report data intelligently. Also this section will aid in understanding how the methods of statistics may be applied to data obtained from section V "Radiochemistry Procedures".

A. COUNTING ERRORS

1. The Standard Deviation - The standard deviation is the basis of all error calculations in radiation counting.

$$\sigma_N = \sqrt{N}$$

Where: σ_N = standard deviation of N

N = observed counts

Therefore if N counts are observed in T minutes, R the count rate $R = \frac{N}{T}$ and the standard deviation σ_R of the count rate equals the square root of the observed counts divided by the time:

$$\sigma_R = \frac{\sqrt{N}}{T}$$

For example, if 40,000 counts are observed in 10 minutes,

Then $N = 40,000$
$T = 10$

$$R = \frac{N}{T} = \frac{40,000}{10} = 4,000 \text{ C min}^{-1}$$

Therefore:

$$\sigma_N = \sqrt{N} = \sqrt{40,000} = 200 \text{ counts}$$
$$\sigma_R = \frac{\sqrt{40,000}}{10} = \frac{200}{10} = 20 \text{ C min}^{-1}$$

Therefore, the true count rate R and the standard deviation of that count rate R is 4,000 C min $^{-1}$ $\pm$ the standard deviation of

A. COUNTING ERRORS (Cont'd)

20 C min^{-1}.

B. CONFIDENCE LEVELS

In the example mentioned above, if we say that the true count rate R = 4,000 C min^{-1} $\pm$20C min^{-1}, we have assigned an error of 1 standard deviation. Statistical principles show that the distribution of errors for a random process such as radioactive decay follows a bell shaped distribution curve. If we assign an error to the observed count rate of 1 standard deviation, the true count rate will on the average lie within the quoted error limits 2/3 or 67 percent of the time. If we assign an error of 2 standard deviations, the true count rate will lie within the stated error limits of 95% of the time. If we assign an error of 3 standard deviations, the true number will lie within the quoted error limits of 99.9% of the time. I would like to point out as long as you understand the probabilities connected with the error you quote, you may use any number of standard deviations you wish.

The relationship between the number of standard deviations and the probability that the true number lies within the error limits quoted is summarized as follows:

Name of Confidence	Probability that the true number lies within the quoted error limits	Number of standard deviations used σ	In c/m equal to
Standard devia.	0.67	1	N/T
95%	0.95	2	2 N/T
99.9%	0.999	3	3 N/T

B. CONFIDENCE LEVELS (Continued)

It is considered good practice in radiation counting to use the two sigma [2σ] error (95% error or 95% confidence level). If you use the two sigma error consistently and the equipment you are using is truly reproducible, you can be confident that the true numbers lie within the quoted error limits 95% of the time. For example, if you observe 900 counts in 15 minutes, the 95% confidence in counts per minute is twice the square root of the number of counts divided by the time or

N = 900 counts, T = 15 minuts, R = 60 c/m

95% conficence = $2\sqrt{N/T} = 2\sqrt{900}/15 = 2\ (30)/15 = 4$ c/m

True count rate R= 60 ± 4 c/m (95% confidence)

C. CHI - SQUARED TEST

When a counter and its electronic components are operating properly, the accuracy in determining the counting rate of a source is limited by the random nature of the disintigration process. If it is not working properly, repeated counts on the same sample will be such that on the average counts will be outside the Chi-square limits.

Chi-square is defined as follows:

$$\text{Chi-square} = \frac{\sum (X_i - \overline{X})^2}{\overline{X}}$$

where:

Xi = observed count for each determination

$\overline{X}$ = mean count (average).

C. CHI - SQUARED TEST (Continued)

The following table shows the allowed limits of Chi-square for different numbers of determinations.

Allowed Limits of Chi-square beyond which it is 99 percent certain that statistical reproducibility is lacking

Number of Determinations	Chi-square limits
5	0.3 - 13
10	2 - 22
15	4 - 29
20	7 - 36
30	14 - 50

CAUTION:

Replicate counts should be made with the same sample and not on supposedly duplicate samples.

An example of Chi-square test where 10 counts were taken:

Determination	Xi	$Xi - \bar{X}$	$(Xi-\bar{X})^2$
1	1069	- 5	25
2	1128	+54	2916
3	1017	-57	3249
4	1023	-51	2601
5	1082	+ 8	64
6	1090	+16	256
7	1030	-44	1936
8	1118	+44	1936
9	1094	+20	400
10	1088	+14	196
	$\sum Xi = 10739$		$\sum (Xi-\bar{X})^2 = 13,579$

$$= \frac{10739}{10} = 1074$$

$$\text{Chi-square} = \frac{\sum (X_i-\bar{X})^2}{\bar{X}} = \frac{13,579}{1074} = 12.6 \text{ for 10 determinations}$$

C. CHI-SQUARED TEST (Continued)

For 10 determinations the Chi-square limits are 2-22, since the above example indicated 12.6 for 10 determinations. Therefore, there is no evidence of any statistical nonreproducibility in the example.

D. PLATEAU DETERMINATION

A plateau is determined by increasing the voltage, the count rate will increase rapidly and then approach a constant value. Further voltage increases result in only slight increases in counting rate, therefore, this region is called the plateau. The end of the plateau is indicated by a second rapid counting rate increase as the region of continuous discharge is reached.

The following is the procedure:

Place a NBS - Radium DEF source in the proportional counter and adjust the high voltage to the point where the counting begins. This is called the starting voltage. Obtain one minute counts at 50 volt increments. See figure I for an example type plateau curve for a flow-type proportional counter.

CAUTION

Do not increase the voltage above the second (Beta plateau on figure I) increase in count rate.

E. COUNTING EFFICIENCY

This portion of section III will show how to determine counter efficiency. Therefore, in order to relate count rates to a dissintegration rate, all measurements should be converted to a

E. COUNTING EFFICIENCY

common base. This base is the absolute disintegration rate of standard calibrated sources. The ratio of the count rate obtained to the distintegration rate of the source is known as the counting efficiency.

PROPORTIONAL COUNTERS

Place the beta or alpha standard in the sample drawer and count for 10 minutes or longer until at least 10,000 counts have been accumulated.

NOTE: For the beta standard, set the voltage on the beta plateau and for the alpha standard set the voltage on the alpha plateau. See section III-D on plateau determination for further information.

Divide the net counts by the time counted.

NOTE: Net counts means total counts minus the background counts. Then divide the counts per minute by the disitegration rate of the standard.

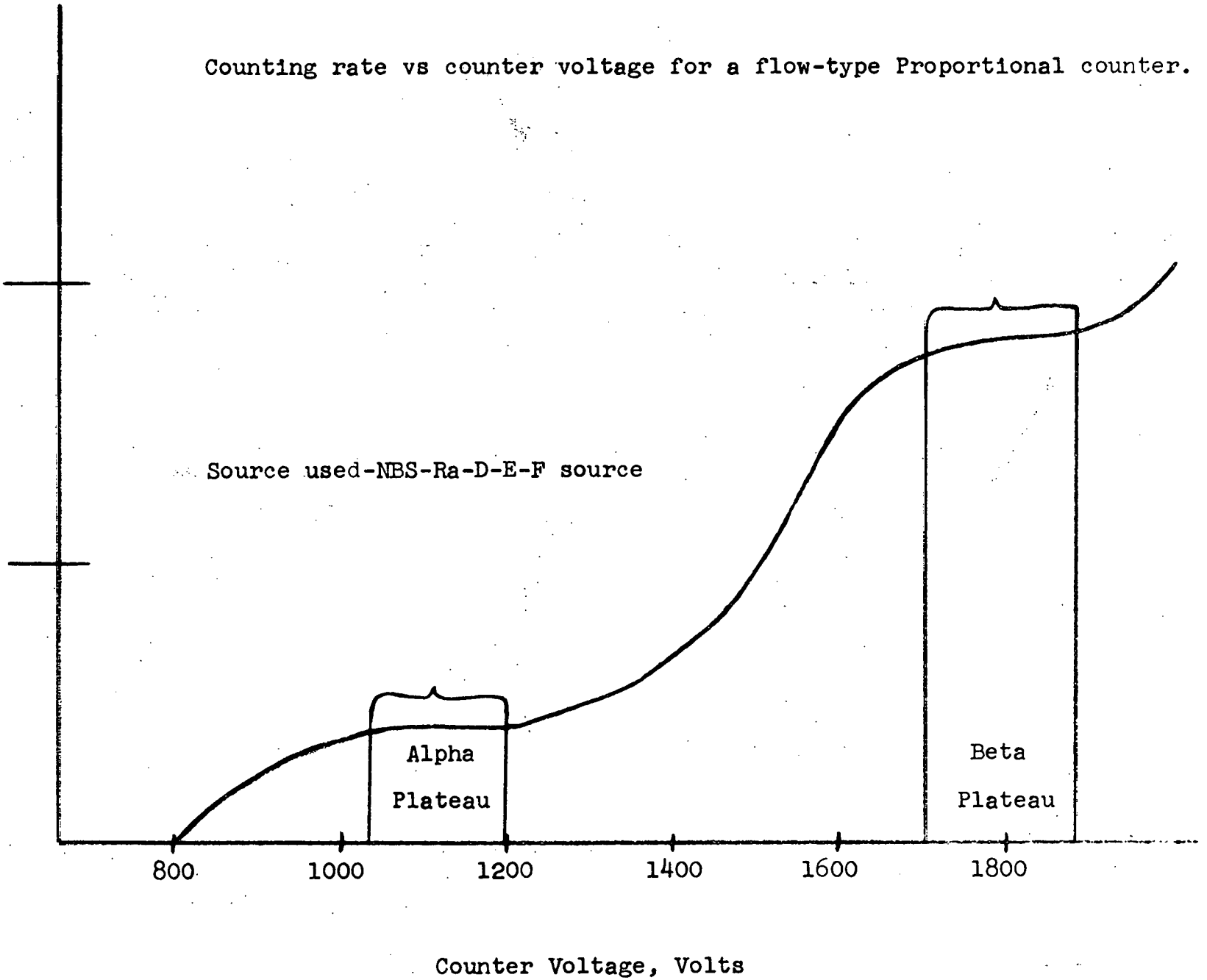
NOTE: The disintegration rate of the standard should be corrected for decay since standardization.

EXAMPLE

A carbon-14 standard with a disintegration rate of $1.1X10^4$ disintegration per minute gives 16,870 counts in 10 minutes. The counter background is 12 counts per minute.

FIGURE I

Counting rate vs counter voltage for a flow-type Proportional counter.



Net counts per minute = $\left(\frac{16,870}{10}\right)$ - (12)

Net cpm = 1675

Therefore the counting efficiency is: eff. = $\frac{1675}{1.1 \times 10^4}$ = .152

GAMMA-RAY COUNTING

Gamma rays are measured by a scintillation counter. Gamma rays from a test sample enter a detector crystal (eg. Na I (Tl) Sodium iodide crystal), transferring all or portions of its energy to it. The crystal then emits light flashes, the number of which is proportional to the energy the crystal received from the sample emitting off Gamma rays. By the use of suitable light sensitive devices and electronic apparatus a pulse is obtained which is related to the disintegration rates of the radionuclides in the sample.

There are two ways to identify an unknown radionuclide by gamma-ray counting type technique. The first method is repeated counting over a period of time and plotting a decay curve on semilog paper of the count rate vs time, which will determine the half-life of the radionuclide. The gamma-ray energy of the radionuclide would be the second method to identify the unknown.

It is desirable to calibrate the multi-channel analyzer so that there is a convenient factor which will convert channel number to Mev (Million electron volts or Kev Kilo electron volts).

To determine the counter efficiency over a range of energies, it is necessary to follow the procedure as outlined below:

GAMMA RAY COUNTING (Continued)

1. Place the following gamma ray standards at various distances and count for a few minutes until at least 10^4 counts have been accumulated.

Nuclide	Energy of gamma-ray (Mev)
Hg-203	0.279
Bi-207	0.569
Cs-137	0.661
Y-88	0.898
Bi-207	1.063
Co-60	1.17
Na-22	1.27
Co-60	1.33
Na-24	1.37
Y-88	1.84
Ti-208	2.61
Na-24	2.76

2. Divide the net counts by the time counted.

NOTE: Net counts means total counts minus the background counts.

3. To determine efficiency factor, divide the counts per minute of the standard by the disintegration rate of the standard.

NOTE: The disintegration rate of the standard should be corrected for decay since standardization.

EXAMPLE

A cesium-137 standard with a disintegration rate of 2.0×10^4 disintegration per minute gives 14,800 counts in 10 minutes. The counter background is 22 counts per minute.

a) The area under the 0.661 photopeak is determined by summing individual channel data over the entire photopeak region (0.661 Mev Cs^{-137}).

Therefore the counting efficiency for Cs^{-137} 0.661 Mev is:

$$\text{Net counts per minute} = \frac{14,800}{10} - (22)$$

Net cpm = 1458

$$\text{Counter Eff} = \frac{1458}{2.0 \times 104} = 7.29 \times 10^{-2}$$

F. DATA REPORT

All sampling, separation and counting data should be reported on Form LACBWR-RW-1. All of the columns may not be needed for every analysis. The one that is needed should be filled in.

The following is the defined terms for the LACBWR-RW-1 form:

Lab-Number - This number should be assigned by the chemistry lab

Sample Number - The designation of the sample shall be written here

Location-Sampling Point - Location on the reactor system, such as the valve number

Analysis Requested - Data needed, such as I-131, Gross Beta, etc.

F. DATA REPORT (Continued)

Sampling

Time - Time when sample was taken

Date - Date when sample was taken

Temperature of Sample - Temperature should be taken immediately after sample has been taken

Activity at Contact - Measure activity using a Cutie-pie or G-M survey meter and report MR/HR at contact

Appearance of Sample - Color and if suspended solids are present

Sample Location Temp. - Temperature of the fluid from which the sample was taken.

Sample Location Flowrate - Flowrate of the fluid from which the sample was taken

Reactor Power Level - Power level during taking the sample

Signature of Samples - The person taking the sample should sign here

Remarks - Any special comments concerning the sample shall be written here.

Separation Data -

Time - The time isotope was separated from the sample taken

Date - The date isotope was separated from the sample taken

Wt. of Sample and Filter - Carrier recovered plus the filter weight. Eg. See method RC-1 Step D-26

Carrier Out - Subtract the wt of filter from the wt of Sample + Filter. Eg. See method RC-1 Step D-27

Carrier In - Carrier added to the sample before separation. Eg. see method RC-1, Step D-1

Aliquote - The amount of sample analyzed shall be entered here. For water samples this shall be in ml and for solid samples in gm.

Total Volume - Total amount of the original sample.

Separation Performed by - The signature of the individual who performed the chemical separation of the sample.

Counting Data - Two columns are available if two isotopes are needed such as iodine-I-131 and I-133 or manganese -Mn-54 and Mn-56.

Isotope - Isotope counted such as I-131, Cr-51 etc.

Instrument - The serial number of the counter used shall be written.

Time - The time of starting the count shall be written here using 24 hour clock.

Date - The day, month and year of counting shall be written here.

Δt - The length of time, in minutes, the sample was counted shall be entered here.

Total Counts - The total number of counts accumulated over the Δt period.

Background counts - The total number of counts accumulated during the counter background determination shall be entered here. This counting time period should be the same as measured during sample counting.

Net Counts - The difference between the total counts and background counts shall be entered here.

R* - Dead time correction for GM tubes shall be entered here.

Absorber - The absorber weight used during counting the sample. Eg: gms/cm2

Shelf - The shelf or distance from the detector the sample was counted

Memory Location - The number of channels used for counting the sample Eg: 1/2 the memory on the Gamma ray spectrometer.

Shelf Factor - The counting efficiency of the sample shall be entered here. For alpha and beta counting this shall be equal to the counting efficiency of the standard. For gamma counting this shall be equal to the counting efficiency of the radionuclide.

Gain - Multi-channel analyzer gain setting.

Counting Performed by - The signature of the individual who performed the counting of the sample.

Form LACBWR-RW-1

Lab-Number	Sample Number	Location-Sampling Point	Analysis-Requested

Sampling

Time _____

Date _____

Purification Operating _____

Temperature of Sample _____

Activity at Contact _____

Appearance of Sample _____

Sample Location Temp. _____

Sample Location Flowrate _____

Reactor Power Level (During Sampling) _____

Signature of Sampler _____

Remarks:

Separation - Data

Time _____

Date _____

Wt of Sample + Filter _____

Wt of Filter _____

Carrier Out _____

Carrier In _____

Aliquote _____

Total Volume _____

Separation performed by _____

Remarks:

Counting - Data

Isotope		Isotope	
Instrument		Instrument	
Time		Time	
Date		Date	
Δ t		Δ t	
Total Counts		Total Counts	
Background Counts		Background Counts	
Net Counts		Net Counts	
R*		R*	
Absorber		Absorber	
Shelf		Shelf	
Memory Location		Memory Location	
Shelf Factor		Shelf Factor	
Gain		Gain	

Counting performed by _____

R* Dead Time Correction

Remarks:

This sheet would be on the reverse side of Form LACBWR-RW-1.

Calculation Sheet

Isotope	Date	Time	Activity C min^{-1}	Chem. Yield (%)	Volume Correction (X)	Photo peak detector Eff. (%)	Gamma Abund-dance (%)	Decay Rate dis. per min. per ml or gm	σR at one stand.Dev

The LACBWR-RW-2 form should be used for counting samples over a period of time for determining decay studies.

The following is the defined terms for the LACBWR-RW-2 form:

Lab number - This number should be assigned by the Chemistry lab.

Sample number - The designation of the sample should be written here.

Instrument counted on - The serial number of the counter and type used shall be written in this space.

Date - The day, month and year of counting shall be written here.

Time - The time of starting the count shall be written here using 24 hour clock

Total Count Rate - The total number of counts accumulated over the ΔT period.

ΔT - The length of time, in minutes, the sample was counted shall be entered here

$C\ min^{-1}$ - The counts per minute shall be entered here

Total Background counts - The total number of background counts accumulated over the background ΔT period.

ΔT Background counts - The length of time, in minutes, the background was counted shall be entered here

C min^{-1} Background - The background counts per minute shall be entered here.

Net $Cmin^{-1}$ - The difference between the total counts and background counts shall be entered here.

Shelf Factor - The counting efficiency of the sample shall be entered here. For alpha and beta counting this shall be equal to the counting efficiency of the standard. For gamma counting this shall be equal to the counting efficiency of the radionuclide.

d min^{-1} Disintegration rate shall be entered here .

Counted By - The initials of the individual who performed the counting of the sample .

LACBWR-RW-2

Counting sheet for Decay Studies

Lab number _____

Instrument counted on _____

Sample number _____

Date	Time	Total count rate	ΔT min	Cmin $^{-1}$	Total Background counts	ΔT Bkg min	Cmin $^{-1}$ Bkg	Net Cmin $^{-1}$	shelf factor	dmin $^{-1}$	Counted By

G. Determination of Half-Life ($t_{\frac{1}{2}}$)

The time interval required for a radioisotope to decay to half its original activity is called the half-life. It may be calculated from:

$$t_{\frac{1}{2}} = \frac{0.693}{\lambda}$$

where:

λ = decay constant for the specific radioisotope.

Therefore to determine the half-life count the sample at one minute intervals. If there does not appear to be a significant difference between successive determinations, count every 10 minutes. After three or more 10 minute counts no significant difference has been observed, use longer periods of time until there is about 5 to 10 percent decrease in activity between successive counts. Using semilog paper plot the net countrate (background has been subtracted) on the logarithmic ordinate and time on the linear abscissa. If a single radionuclide is present, a straight line will be observed as shown in figure II. If two radionuclide are present, a straight line will not be observed but a curve with two components as shown in figure III will be observed. If there are more than two radionuclides, this method will not be too accurate, necessitating a radiochemical separation to determine accurately the radionuclides present. Once the half-life is determined, a tentative identification of the nuclide on a single and a two component unknown sample may be made using the General Electric chart of the Nuclides or similar type chart. More positive

FIGURE-II

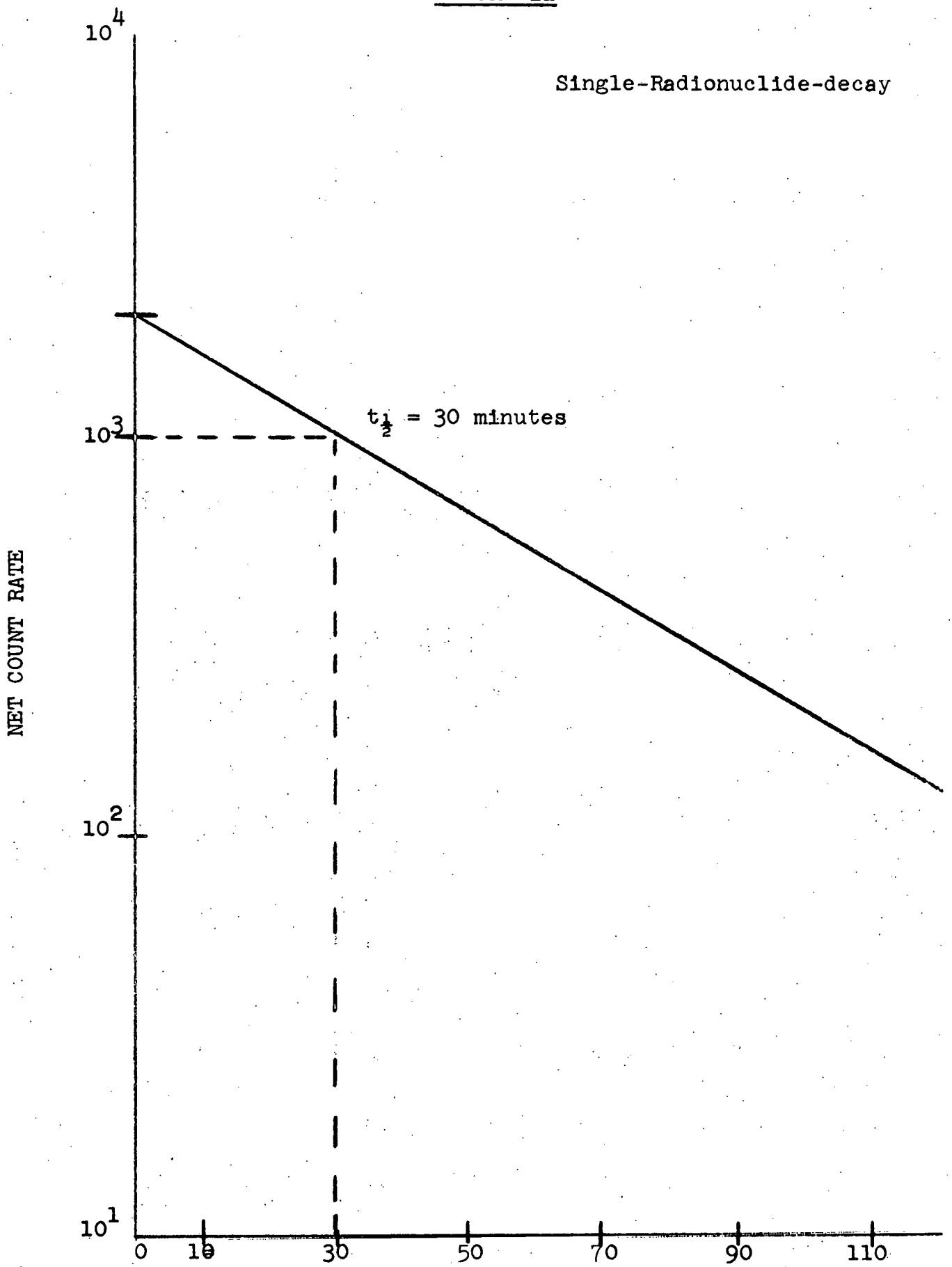
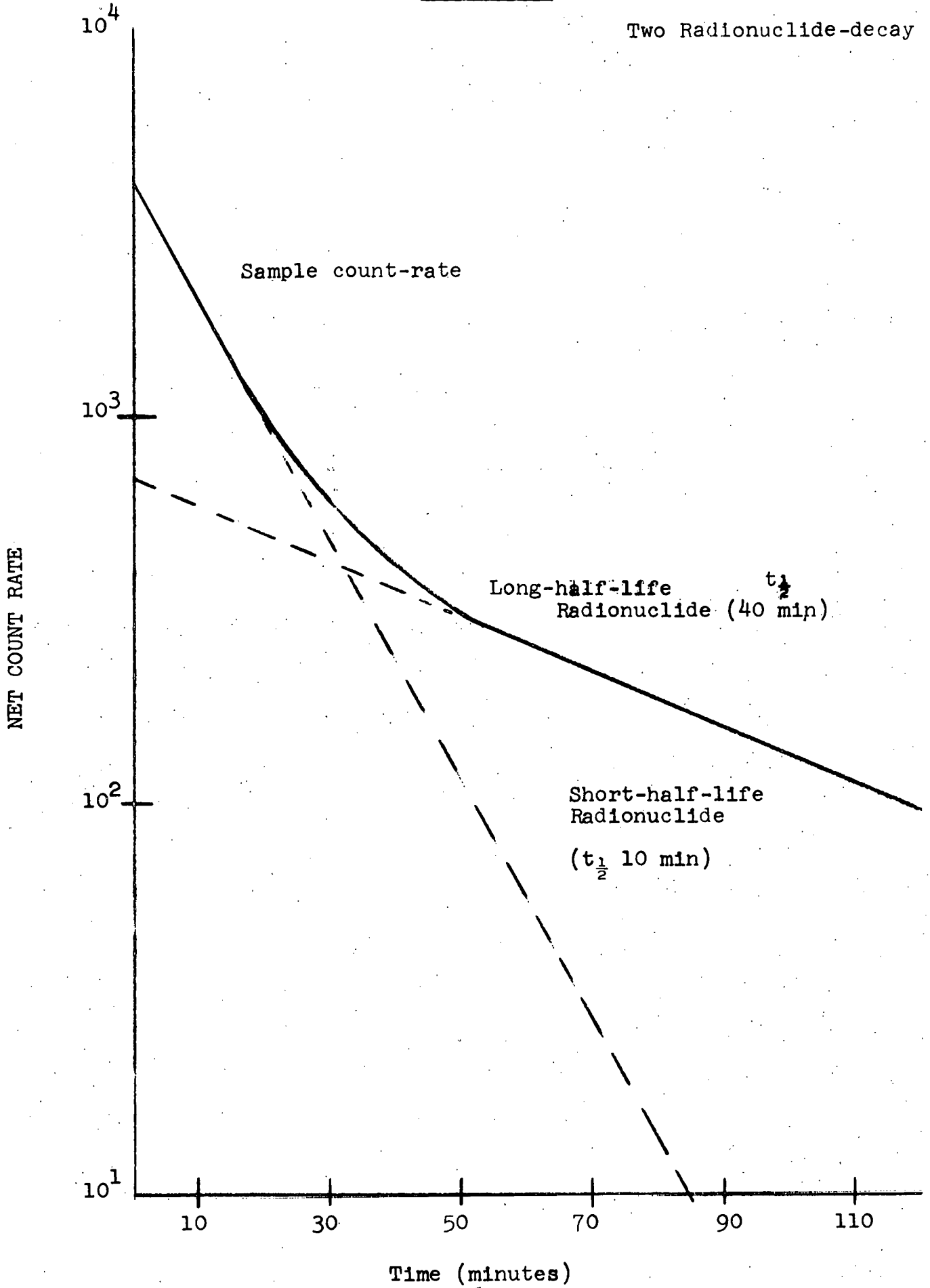

Single-Radionuclide-decay
10^4
10^3
10^2
10^1
$t_{\frac{1}{2}}$ = 30 minutes
NET COUNT RATE
0
10
30
50
70
90
110
Time (minutes)

FIGURE III


Two Radionuclide-decay
Sample count-rate
Long-half-life Radionuclide (40 min)
Short-half-life Radionuclide
($t_{\frac{1}{2}}$ 10 min)
NET COUNT RATE
10^4
10^3
10^2
10^1
10
30
50
70
90
110
Time (minutes)

G. Determination of Half-Life ($t\frac{1}{2}$) (continued)

identification can be made from the beta and gamma energies as determined by a Feather analysis, radiochemical separation and a gamma spectrum.

H. RADIOACTIVE DECAY CORRECTIONS

To correct to the initial activity Ao, the procedure below should be followed:

Divide the elapsed time between counting and sampling by the half-life of the radionuclide which has been determined by using the method mentioned in Section II-G. Using figure IV and knowing the number of $t\frac{1}{2}$ (half-life) the sample has decayed the value $(\frac{A}{A_o})$ fraction of activity remaining can be read off the logarithmic ordinate of figure IV.

Divide the activity by the $\frac{A}{A_o}$ value to obtain the initial activity.

To explain this better I will show how a typical problem can be performed.

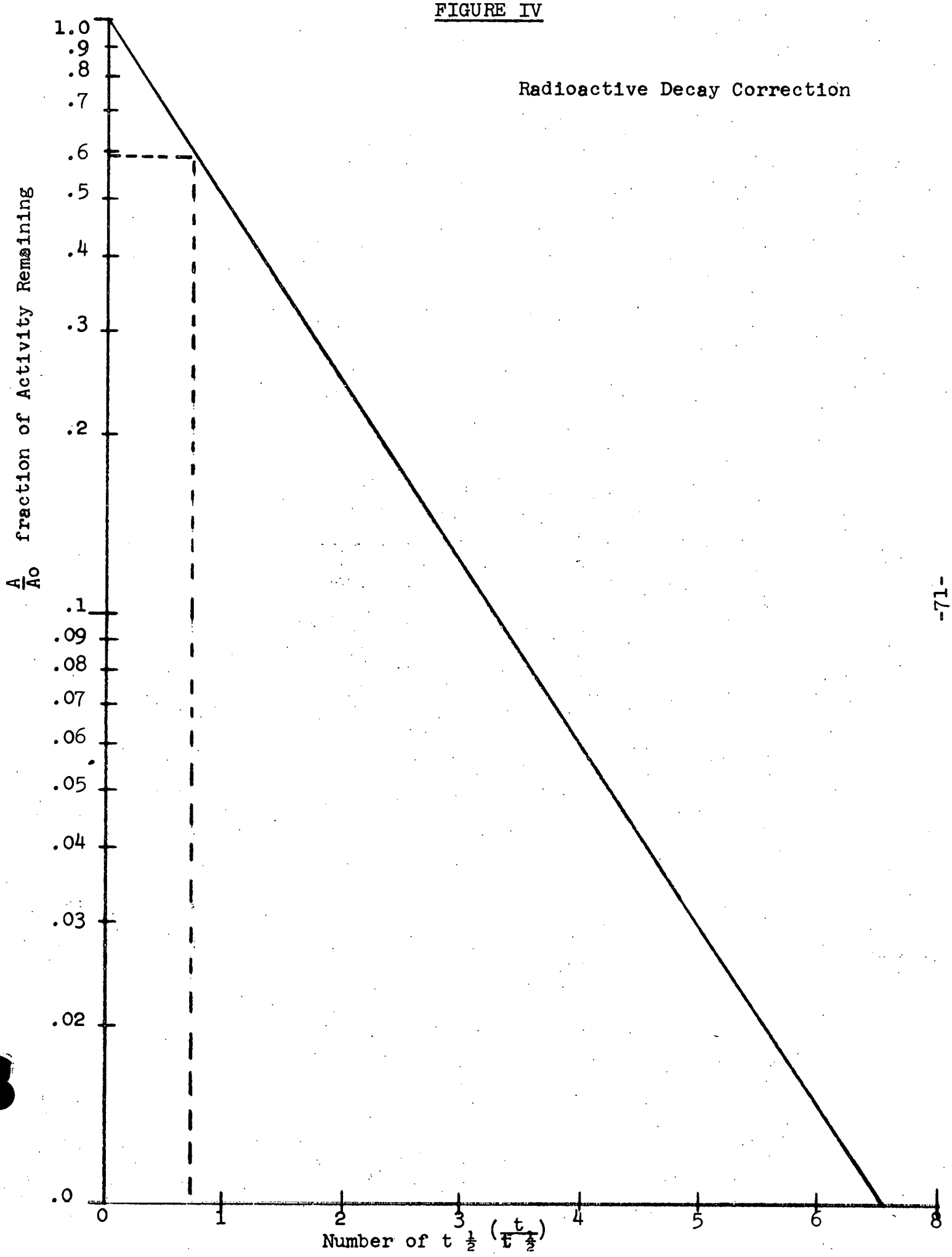
A sample was taken from the reactor system on January 1 (0600 hrs.) and the separated sample was counted for I-131 (1000 C min^{-1}) on January 7 (0600 hrs.).

The half-life of I-131 - 8.05 days time from sampling to counting time - 6 days

Therefore divide: $\frac{t}{t\frac{1}{2}} = \frac{6 \text{ days}}{8.05 \text{ days}} = 0.746$

FIGURE IV

Radioactive Decay Correction



H. RADIOACTIVE DECAY CORRECTIONS (Continued)

Using figure IV read on the abscissa 0.746 and find $\frac{A}{A_o}$ on the logarithmic ordinate (see figure IV for illustration)

$\frac{A}{A_o} = .59$

The activity at sampling time is:

$$\frac{1000 \text{ c min}^{-1}}{.59} = 1695 \text{ c min}^{-1}$$

Using a slide rule the sample problem above can be solved by multiplying λ times t and reading the LL02 scale for the e^- value.

EXAMPLE:

Where $A = Aoe^{-\lambda t}$

$1000 \text{ cpm} = Aoe^{-(.0862)} \quad (6.0 \text{ days})$

$\lambda = \frac{.693}{8.05 \text{ days}} = .0862$

Therefore using a slide rule place 1 on the C scale over the D scale 862 and then moving the hairline to 6 on the C scale, read the LL02 scale. The reading should be .596.

I. FEATHER ANALYSIS

This type analysis identifies the Beta energy or energies of an unknown radioactive sample. To identify the unknown sample by its beta energies the following procedure should be followed: Place the sample in the proportional flow counter or under

the G-M counter and count for 10 minutes with no absorber and with aluminum absorbers of approximately 5 to 3500 mg/cm^2 thicknesses. (Background should be subtracted for each measurement).

CAUTION: To carry out these measurements, the aluminum absorbers are to be placed as near to the counting tube as possible to minimize scattering effects.

Calculate the total absorber for each measurement by adding to the aluminum absorber the thickness in mg/cm2 of the counting tube window and the air between the sample and the counting tube.

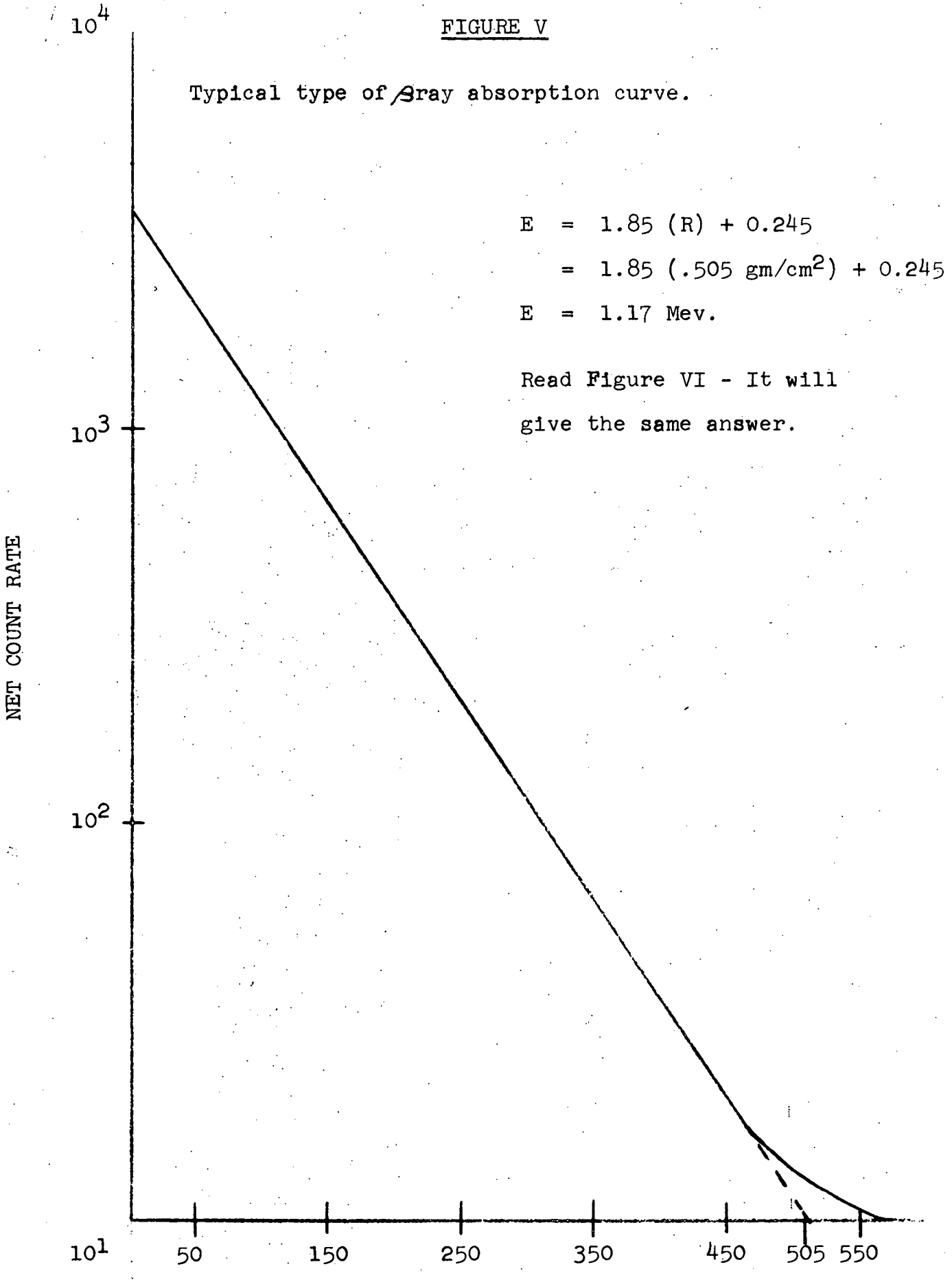
NOTE: This is equal to the distance in cm times the density of air in mg/cm2 at the ambient temperature, pressure and humidity. (This information can be found in the Handbook of Chemistry and Physics for these densities). Normally this correction is made when extreme accuracy is necessary.

Using semi-log paper, plot the count rate on the logarithmic ordinate vs the absorber on the linear abscissa as shown in figure V, and the maximum range is taken as the absorber thickness at which the curve flattens out to the constant background.

See figure VI for the Beta particle range energy curve.

FIGURE V

Typical type of βray absorption curve.



$E = 1.85 (R) + 0.245$

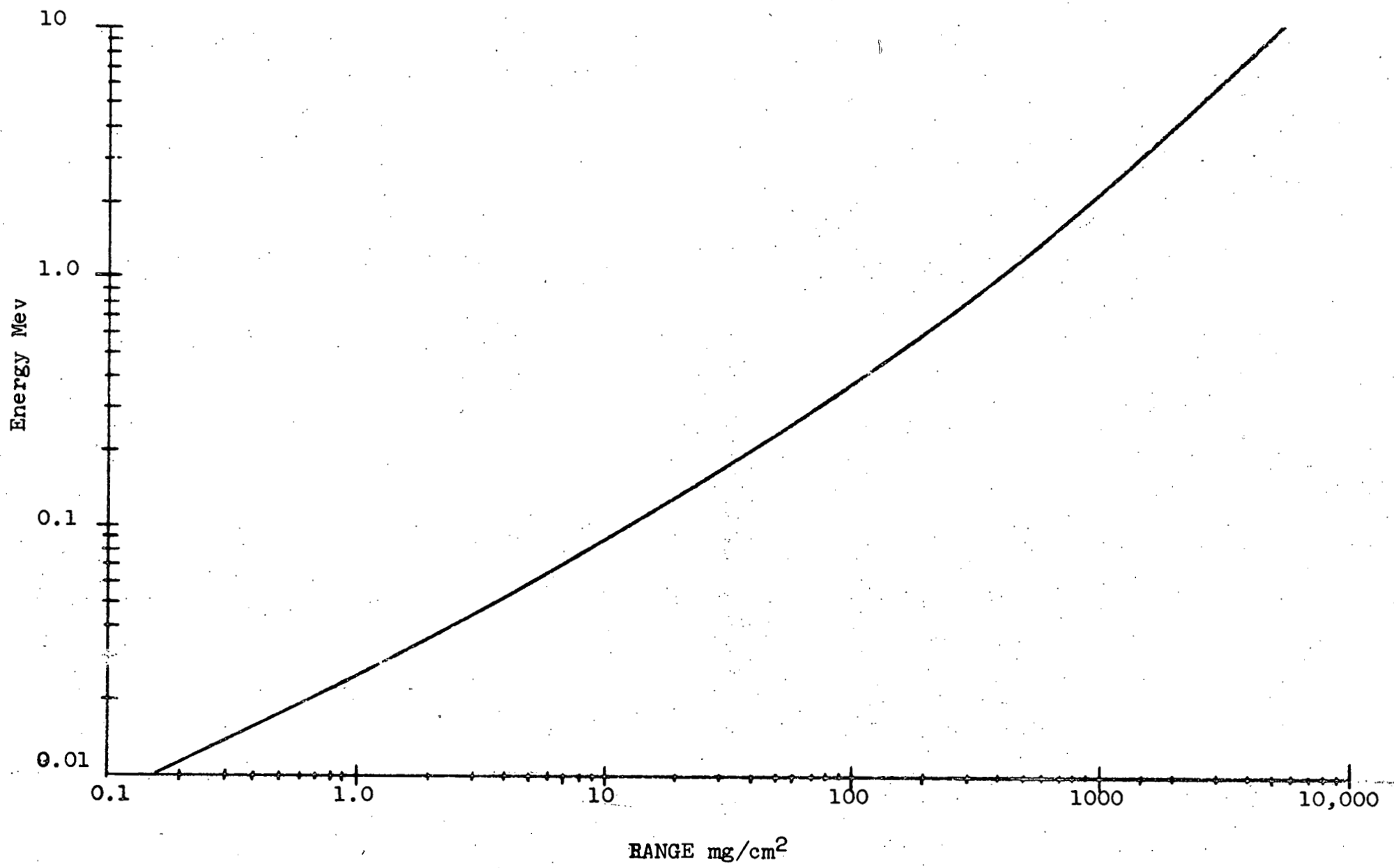
$= 1.85 (.505 \text{ gm/cm}^2) + 0.245$

$E = 1.17$ Mev.

Read Figure VI - It will give the same answer.

FIGURE VI

Beta Particle Range Energy Curve



SECTION IV

WATER CHEMISTRY METHODS

Section IV is a collection of water chemistry procedures for determining constituents in reactor steam and water. The method specified for these analyses was chosen on the accuracy and simplicity of the method. The methods have been taken from ASTM and various established methods throughout the industry.

P^H DETERMINATION

Method No. WC 1

A. SUMMARY OF METHOD

The hydrogen ion Concentration is indicated by a P^H measurement which may be made with electrical instruments.

B. APPARATUS

1. Beckman Zeromatic P^H meter or equivalent
2. Glass electrode
3. Calomel reference electrode
4. Temperature Compensation Probe
5. Normal laboratory glassware is required for this work.

C. REAGENTS AND MATERIALS

1. Standard set of buffer solution P^H-1-14 @ 25°C.

D. PROCEDURE

1. Slide rubber sleeve down to expose vent hole on the referency electrode. Rinse the electrodes with demineralized water and wipe dry.

   NOTE: Instrument should have a warm up period of 15-30 minutes.
2. Standardize P^H meter using standard buffer solutions whose P^H value is close to that expected in the sample.
3. Immerse the electrodes in one buffer solution, depress READ button and adjust the ASYMETRY CONTROL to set the meter needle

PROCEDURE (Cont'd)

to exactly read the P^H of the rating stated for the buffer solution.

4. Depress STANDBY button, remove electrodes, wash electrodes with demineralized water and wipe dry.
5. Repeat step 4.1.4.3 and 4.1.4.4 using a different buffer P^H range.
6. Insert electrodes into sample and let stand for a few minutes, depress READ button and read P^H on meter.

   NOTE: Sample should be approximately at room temperature
7. Cover vent hole upon completion of test.

E. CALCULATIONS

None

F. PRECAUTIONS

1. Leave the instrument connected to the power line except when not to be used for extended periods.
2. Depress STANDBY button when the instrument is not in use, and whenever removing the electrodes.
3. It is essential to standardize the instrument at least daily with the buffer solution.
4. A new glass electrode should be soaked in water for several hours before use. If stored in water it is ready for immediate use. Be certain the Calomel reference electrode

PRECAUTIONS (Cont'd)

is filled with saturated K Cl solution, and contains K Cl crystals. The electrode may be temporarily stored in demineralized water. The long periods of storage, store in saturated K Cl solution.

CONDUCTIVITY DETERMINATION

(Dip Cell Method)

Method No. WC-2

A. SUMMARY OF METHOD

A dip cell is immersed in the sample water and the conductivity is read directly from a bridge type instrument.

B. APPARATUS

1. RD-327 Solu Bridge
2. Cel-A-002 Dip Cell

NOTE: The RD-327 Solu Bridge conductivity scale is calibrated, and is direct reading, for use with a cell that has a cell constant of 2. The dip cell being used has a cell constant of 0.02. Therefore, it is necessary to multiply the scale reading obtained by 0.01 to correct for the use of a cell with a lower cell constant.

3. 250 ml Erlenmeyer flask - 2 each

C. REAGENTS AND MATERIALS

1. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D1193).

D. PROCEDURE

1. Connect the dip cell leads to the terminals at the bottom of the Solu Bridge.
2. Plug line cord into 120 volt outlet
3. Transfer solution to be tested into a 250 ml Erlenmeyer flask.
4. Remove dip cell from storage flask and place in the solution to be tested. Move the cell up and down under the solution until all air bubbles inside the cell casing or shield are removed. Immerse the cell to a point at least $\frac{1}{2}$" above the air vents. Alloy at least $\frac{1}{2}$" clearance at the sides and bottom.

   NOTE: The cell is normally stored in a 250 ml Erlenmeyer flask in demineralized water.
5. Turn the switch to the ON position and allow about 30 seconds for warm up.
6. Measure the temperature of the solution with a thermometer, and set the pointer of the temperature scale to the corresponding value.
7. Rotate the pointer of the conductivity scale until the black segment of the electron ray tube reaches its widest opening. The bridge is now at balance. The scale is read and the reading multiplied by 0.01 to determine the conductivity.

E. CALCULATIONS

Direct reading from the instrument. See step D-7 for determining the conductivity of the sample.

CHLORIDE DETERMINATION

Method No. WC-3

A. SUMMARY OF METHOD

The chloride ion reacts with the mercuric thiocyanate to produce thiocyanate ion to form red ferric thiocyanate. The intensity of the color, which is proportional to the concentration of the chloride ion, is measured photometrically at a wave length of 463 mμ using a 10 cm cell. This method is good in the range of 0.02 to 10 ppm chloride ion.

B. APPARATUS

1. Spectrophotometer - Beckman DU Spectrophotometer is preferred.
2. Normal laboratory glassware is required for this work

C. REAGENTS AND MATERIALS

1. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D1193).
2. Ferric Solution - Dissolve 5.0 g of ferrous ammonium sulfate $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 20 ml of water. Add 38 ml of concentrated nitric acid and boil to oxidize the iron and remove the oxides of nitrogen. Dilute to 100 ml with halide free water.
3. Mercuric thiocyanate, methanol solution (3 g per liter) - Dissolve 0.30 grams of mercuric thiocyanate in 100 ml of

methanol. Store in amber bottles. Allow to stand for at least 24 hours before using.

CAUTION: Do not use if more than four weeks old.

4. Sodium chloride standard solution (10 mg Cl per liter) - Dry sodium chloride (NaCl) to constant weight at 105° C. Prepare a stock solution by dissolving exactly 1.649 grams of the dry NaCl in water and dilute to 1 liter. Prepare the standard solution as needed by diluting 10 ml of the stock to water with chloride free water. The resulting standard contains 10 mg of chloride ion per liter.
5. 15.7N Nitric Acid - concentrated Nitric acid (HNO_3)

D. PROCEDURE

CAUTION: Soak all new glassware in hot (1-20) nitric acid (HNO_3) for several hours. To be certain that new glassware is conditioned for the test, run a chloride determination on halide free water. After the run, rinse the glassware thoroughly. Soak the glassware in halide free water between tests. Discard all glassware that appears etched or scratched.

1. Prepare series of reference standards by diluting suitable volumes of the standard chloride solution with halide free water. The series should cover the range from 0.02 ppm to 10 ppm.

NOTE: The temperature of the solutions used for calibration must be the same as that of the sample tested.

PROCEDURE (Cont'd)

2. Transfer 25 ml of sample to a glass-stoppered volumetric flask or bottle.
3. To each of the calibration standards and samples add 5 ml of ferric solution and 2.5 ml of mercuric thiocyanate solution.
4. Shake thoroughly for 1 or 2 minutes and allow to stand for 10 minutes.
5. Measure the intensity of the color formed using the DU Spectrophotometer.

   NOTE: Adjust the zero setting of the spectrophotometer by using 25 ml of halide free water tested in accordance with steps D3 and D4.

E. CALCULATIONS

Prepare a calibration curve by plotting the readings on the photometer versus the concentration of chloride. When the scale of the photometer reads directly in absorbance, plot the curve on rectilinear paper. When the scale reads in transmittance, it is convenient to plot the results on semi-log paper, using the single cycle log axis to plot transmittance and the linear axis to plot concentrations.

IRON DETERMINATION

Method No. WC-4

A. SUMMARY OF METHOD

Iron is determined photometrically as the orange-red complex at about P^H 4.0. Measurement is made at 510 mμ on the DU spectrophotometer using a 1 cm cell.

B. APPARATUS

1. Spectrophotometer - Beckman DU Spectrophotometer is preferred.
2. Normal laboratory glassware is required for this work.
   NOTE: Rinse all glassware in concentrated hydrochloric acid (HCl).

C. REAGENTS AND MATERIALS

1. Purity of Reagents - Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.
2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D1193).

REAGENTS AND MATERIALS (Cont'd)

3. 6N Hydrochloric Acid - Measure 498 ml of (12.1N) Hydrochloric Acid and dilute to 1-liter with water.
4. 4N Hydrochloric Acid - Measure 232 ml of (12.1N) Hydrochloric Acid and dilute to 1-liter with water.
5. Hydroylamine Hydrochloride Solution - Dissolve 10 grams of hydroxylamine hydrochloride (NH_2OH. HCl) in a small quantity of water and dilute to 100 ml. This solution is stable for several months.
6. Orthophenanthroline (1-10-phenanthroline) Solution - Dissolve 0.1 gram of the orthophenanthroline in 10 ml of ethyl alcohol, and dilute to 100 ml with water. The solution should be discarded if it darkens.
7. Acetate Buffer Solution - Dissolve 50 grams of ammonium acetate, $NH_4C_2H_3O_2$ in 50 ml of demineralized water. Add 100 ml of Glacial Acetic acid, and dilute to 500 ml with water.
8. 3N Ammonium Hydroxide - Measure 202 ml of concentrated (14.8N) ammonium hydioxide (NH_4OH) and dilute to 1-liter with water.
9. Standard Iron Solution (1ml=0.1000 mg Fe) - Weigh 0.1000 gram of electrolytic "iron wire for standardizing" and place in a 50 ml beaker. Dissolve in 20 ml of 4N hydrochloric acid (HCl) while heating gently on a hot plate. Transfer to a 1-liter volumetric flask using water and dilute to 1-liter with water.

REAGENTS AND MATERIALS (Cont'd)

10. 10 ppm Iron Standard Solution - Measure accurately 10 ml of the C-9 stock solution and dilute to 100 ml with water. (Use volumetric flask for this operation).

D. PROCEDURE

1. Pipet 1, 5, 10 and 50 ml aliquots of the C-10 iron standard solution into separate 250 ml Erlenmeyer flasks. Also prepare a blank with no iron standard added.

   NOTE: The iron solution aliquots represents iron concentrations of 0.10, 0.50, 1.0 and 5.0 ppm respectively.

2. To each sample add 1 ml of 6N hydrochloric acid (HCl) and boil on a hot plate for 5 minutes and cool in a water bath.
3. To each sample add 1 ml of hydroxylamine hydrochloride and mix by swirling the solution in the Erlenmeyer flasks for approximately 1 minute.
4. Add 5 ml Orthophenanthroline to each flask, and swirl flask to mix solution.
5. Add 5 ml acetate buffer to each flask.
6. Dropwise, add 3N ammonium hydroxide (NH_4OH) to a p^H of 3.5 to 4.0 is reached or to make Congo-red indicator paper red.
7. Quantitatively transfer the samples to 100 ml volumetric flasks and dilute to volume mark with water and shake for 1 or 2 minutes. Allow to stand for 15 minutes for full color development.

REAGENTS AND MATERIALS (Cont'd)

8. Read the transmittance on the DU Spectrophotomer at 510 mμ using 1 cm cells.

9. Secure a fresh sample (sample needed to be analyzed for iron content) and pipet a 50 ml aliquot into a 250 ml Erlenmeyer flask.

   NOTE: Prepare samples for analysis as follows:

   1. Primary water - none
   2. Crud - Fume aliquot to eliminate all interfering acids.

      NOTE: If allowed to bake, black MnO_2 precipitates. Add some demineralized water plus 6N hydrochloric acid (HCl) plus one drop of 30% Hydrogen Peroxide to reduce the Maganese. Boil off the peroxide. Manganese concentration should not exceed 2 mg/25ml final volume.

10. Repeat steps D-2, D-3, D-4, D-5, D-6 and D-7.

11. Repeat Step D-8 and obtain Fe concentration from curve produced on steps E-1.

E. CALCULATIONS

1. Plot the reading from step D-8 versus concentration of iron (ppm in 100 ml) on semi-log paper.

   NOTE: This plot should be a straight line.

Total Iron (ppm) = standard curve reading (ppm) $\frac{(100\ ml)}{\text{sample volume (ml)}}$

SUSPENDED SOLIDS DETERMINATION

Method No. WC-5

A. SUMMARY OF METHOD

The suspended solids is determined by filtering the sample through a Millipore filter.

B. APPARATUS

1. Normal laboratory glassware is required for this method.
2. Filter - Millipore type HA filter (47 mm).
3. Stainless filter holder - hydrosol stainless filter holder Cat No. XX20-047-20 Millipore Co.
4. Graduated Cylinder - 1000 ml capacity.
5. Desiccator - The desiccator should be similar to Fisher No. 8-615.
6. Oven - Oven should be gravity convection type and be able to supply uniform heat at $110^{o}C \pm 0.5^{o}C$.
7. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

C. REAGENTS AND MATERIALS

None

D. PROCEDURE

1. Dry a Millipore type HA filter in an oven at $110^{o}C \pm 5^{o}C$ for 2 minutes.
2. Place the filter into a desiccator and cool.

PROCEDURE (Cont'd)

3. Weigh the filter to the 0.10 mg on the analytical balance.
4. Repeat steps D-1, D-2 and D-3 until content weight is obtained.
5. Place the filter in the one liter stainless steel filter holder.
6. Measure 1000 ml of the sample using a graduated cylinder and vacuum filter through the filter holder.

   CAUTION: The filtrate should be collected in a clean 1000 ml filter flask. Also save the filtrate for further analysis.
7. Remove the filter and dry in an oven at $110^{o} \pm 5^{o}C$ and repeat steps D-2, D-3 and D-4.

E. CALCULATIONS

$$\text{Suspended Solids (ppm)} = \frac{1000\ (W_2 - Wi)}{V}$$

where:

Wi = initial weight of filter in mg.

W_2 = final weight of filter plus suspended solids in mg.

V = volume of samples in milliliters.

DISSOLVED SOLIDS DETERMINATION

Method No. WC-6

A. SUMMARY OF METHOD

The dissolved solids are determined by evaporation of a known volume of a filter sample from procedure WC-5 in a tared evaporating dish.

B. APPARATUS

1. Normal laboratory glassware is required for this work.
2. Evaporating Dish - 150 ml size, pyrex or equivalent glass should be used.
3. Desiccator - The desiccator should be similar to Fisher No. 8-615.
4. Oven - Oven should be gravity convection type and be able to supply uniform heat at $110^{o}C \pm 0.5^{o}C$.
5. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

D. PROCEDURE

1. The filtrate collected in step D-6 of the WC-5 method is used to determine dissolved solids.
2. Clean a pyrex evaporating dish by washing carefully in cleaning solution or a good detergent cleaning compound. Rinse thoroughly with demineralized water.
3. Dry and place in oven at $105\text{-}110^{o}C$ for several hours. Cool in desiccator until dish is at room temperature. Weigh dish to nearest 0.10 mg on the analytical balance.

PROCEDURE (Cont'd)

NOTE: Handle dish only with tongs to avoid grease from hands.

4. Pipet a 1000 ml sample into the evaporating dish and evaporate almost to dryness on a low heat. A ribbed watch glass should be placed over the evaporating dish to exclude dust during evaporation.
5. Transfer the dish to an oven set at 110°C ± 5°C and continue evaporation until dryness. Dry for two additional hours. Cool in desiccator.
6. Determine weight of dish plus residue to the nearest 0.10 mg on the analytical balance.

E. CALCULATIONS

$$\text{Total solids (ppm)} = \frac{1000\ (W_2 - Wi)}{V}$$

where:

Wi = initial weight of dish in milligrams

W_2 = final weight of dish in milligrams

V = volume of samples in milliliters.

TOTAL SOLIDS DETERMINATION

Method No. WC-7

A. SUMMARY OF METHOD

The total solids are determined by evaporation of a known volume of sample in a tared evaporating dish.

B. APPARATUS

1. Normal laboratory glassware is required for this work.
2. Evaporating Dish - 150 ml size, pyrex or equivalent glass should be used.
3. Graduate Cylinder or 100 ml pipette
4. Desiccator - The desiccator should be similar to Fisher No. 8-615.
5. Oven - Oven should be gravity convection type and be able to supply uniform heat at 110°C ± 0.5°C.
6. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

C. REAGENTS AND MATERIALS

None

D. PROCEDURE

1. Clean a pyrex evaporating dish by washing carefully in cleaning solution or a good detergent cleaning compound. Rinse thoroughly with demineralized water.
2. Dry and place in oven at 105-110°C for several hours. Cool in

PROCEDURE (Cont'd)

desiccator until dish is at room temperature. Weigh dish to nearest 0.10 mg on the analytical balance.

NOTE: Handle dish only with tongs to avoid grease from hands.

3. Pipet a 100 ml sample into the evaporating dish and evaporate almost to dryness on a low heat. A ribbed watch glass should be placed over the evaporating dish to exclude dust during evaporation.

   NOTE: To evaporate large volume samples a Evaporator Feeder used in Method RC-14 can be used.

4. Transfer the dish to an oven set at 105-110°C and continue evaporation until dryness. Dry for two additional hours. Cool in desiccator.

5. Determine weight of dish plus residue to the nearest 0.10 mg on the analytical balance.

E. CALCULATIONS

$$\text{Total solids (ppm)} = \frac{1000\ (W_2 - Wi)}{V}$$

where:

Wi = initial weight of dish in milligrams

W_2 = final weight of dish in milligrams

V = volume of samples in milliliters.

DISSOLVED OXYGEN IN WATER

Method No. WC-8A

A. SUMMARY OF METHOD

Dissolved oxygen reacts under alkaline conditions with the indigo carmine solution to produce a color change from yellow-green through red to blue and blue-green. The result of each test can be determined by comparison of color developed in the sample with a color comparator

NOTE: This method is applicable to water containing 0-30 ppb and 0-300 ppb of dissolved oxygen, using two separate comparators.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Buret - a 25 or 50 ml buret.

3. Sampling Bucket - The sampling bucket with an overflow at least 1 inch above the top of the sampling vessel.

4. Sampling Vessels - Nessler-type tubes or 300 ml BOD bottles have a raised lip around the neck and glass stoppers ground to a conical lower tip.

5. Oxygen Comparator III - The comparator consists of a rotating six color disc and support for BOD sample bottel. This disc has matching colors for six quantities of oxygen

B. APPARATUS (Cont'd)

and will rotate to expose one color at a time. The values are 0, 5, 10, 15, 20 and 30 ppb as oxygen. This item can be purchased from R.L. Johnson, 2780 Brookside, Jackson, Michigan.

6. Oxygen Comparator IV - Same as B-5 accept the values are 10, 25, 50, 75, 150 and 300 ppb as oxygen. This item can be purchased from the same company.

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the specification for Reagent Water (ASTM Designation D 1193).

3. 12.1N Hydrochloric Acid - Concentrated hydrochloric acid (HCl).

C. REAGENTS AND MATERIALS (Cont'd)

4. (1-99) Hydrochloric Acid - Mix 1 volume of concentrated hydrochloric acid with 99 volumes of water.

5. Indigo Carmine Solution - Dissolve 0.18 gram of 100 percent indigo carmine and 2.0 gram of dextrose (or glucose) in 50 ml of water. Add 750 ml of glycerin and mix thoroughly.

NOTE: The solution is usable for at least 30 days if stored in a refrigerator.

CAUTION: The stock solution deteriorates rapidly if allowed to stand in a lighted room at ambient temperature in an ordinary reagent bottle.

6. Potassium Hydroxide Solution - Dissolve 530 grams of potassium hydroxide (KOH) in water and dilute to 1-liter with water.

NOTE: Store in refrigerator.

7. Indigo Carmine - Potassium Hydroxide Reagent - Mix four parts by volume of C-5 solution (indigo carmine solution) with one part of C-6 solution (potassium hydroxide solution). Mix solution for several minutes.

NOTE: Allow the reagent to stand undisturbed until the initial red color changes to lemon yellow.

C. REAGENTS AND MATERIALS (Cont'd)

CAUTION: Keep in a dark cool place. Prepare a fresh solution daily.

D. PROCEDURE

1. Mount a buret directly above the B-4 sampling vessel neck so that the buret tip dips into the overflowing sample to a depth of about 1/2 inch.

2. Fill the buret with indigo carmine-potassium hydroxide reagent to about 1 ml above the zero mark.

3. Drain the buret to the zero mark into the overflowing sample, and allow the sample to flush for 1 minute longer.

4. Remove the sample tubing gently so as not to introduce air bubbles and quickly introduce 0.8 ml of indigo carmine-potassium hydroxide reagent from the buret into the sample if a 60 ml Nessler-type tube is used.

NOTE: If a BOD bottle is used add 4 ml of the reagent.

5. Raise the buret above the sample vessel and immediately stopper the vessel firmly with a rinsed glass stopper, being carefuly to exclude air bubbles.

6. Invert the vessel several time to mix.

NOTE: A color indicative of the dissolved oxygen concentration will develop.

E. CALCULATIONS

1. Place the sample vessel on a white surface and match its color with the oxygen comparators from step B-5 and B-6.

2. Equivalent dissolved oxygen can be read using the values recorded on each comparator.

CAUTION: Colors should be matched as soon as possible after mixing the reagent and sample, since the colors are not stable for more than 30 minutes and air leakage may cause a change in color.

DISSOLVED OXYGEN IN WATER

Method No. WC-8B

A. SUMMARY OF METHOD

The sample is collected in a BOD bottle. The free iodine liberated in an amount equivalent to the oxygen in the sample is titrated with thiosulfate using starch as an indicator.

NOTE: This method is applicable to water containing more than 0.05 ppm of dissolved oxygen.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Sample Bottle - One 300 ml BOD bottle having a raised lip around the neck and a glass stopper ground to a conical lower tip.

   NOTE: The capacity of the bottle must be measured to the nearest ml and the stopper should be tied to the neck of the bottle with a loop of cord.

3. Casserole - A 1-liter glazed porcelain casserole, clear white in color.

4. Pipets - Three 2 ml transfer pipets and serological pipets of 1.00 and 5.00 ml capacities, graduated in 0.01 and 0.10 ml divisions, respectively.

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the specification for Reagent Water (ASTM Designation D 1193).

3. Manganous Sulfate Solution - Dissolve 364 gms of manganous sulfate ($MnSO_4 \cdot H_2O$) in water, filter and dilute to 1-liter with water.

4. Potassium Iodide (Alkaline Solution) - Dissolve 700 gms of potassium hydroxide (KOH) in sufficient water to make approximately 700 ml of solution in a 1-liter volumetric flask (cool to room temperature). Dissolve 150 gms of iodate-free potassium iodide (KI), in 200 ml of water and mix with the KOH solution in the volumetric flask. Dilute to 1-liter with water and shake for 1 or 2 minutes. CAUTION: Store solution in a dark, rubber-stoppered bottle.

C. REAGENTS AND MATERIALS (Cont'd)

5. (0.1N) Sodium Thiosulfate Standard Solution - This can be purchased from Fisher as a certified standard - Cat. So-S-368. It is standardized against National Bureau of Standards Potassium Dichromate.

6. (3-1) Sulfuric Acid - Pour carefully 750 ml of concentrated sulfuric acid (H_2SO_4) into 250 ml of water in a beaker which is placed in a sink. Cool to room temperature transfer to a 1-liter volumetric flask and dilute to 1-liter with water.

7. Starch Indicator - This indicator is available from Fisher - Cat. No. SO-S-408.

D. PROCEDURE

1. Fill a 2 ml transfer pipet with alkaline potassium iodide solution and with the pipet filled to the tip so that no bubble of air will be forced into the sample, ease the bottle stopper out of its seat and simultaneously thrust the pipet tip past it and into the neck of the bottle.

2. Allow the contents of the pipet to drain into the bottle and stopper bottle after the pipet is drained.

3. Fill another 2 ml pipet with manganous sulfate solution and add to the sample in the same way as described in steps D-1 and D-2.

D. PROCEDURE (Cont'd)

4. Stopper tightly and shake the bottle to mix the contents thoroughly.

5. Allow the bottle to stand and when the precipitate has settled below the shoulder of the bottle, add 2 ml of (3-1) sulfuric acid in the same way described in step D-1 and D-2.

6. Stopper and shake until all precipitate is dissolved.
   CAUTION: Steps D-1 through D-6 should be completed within 15 minutes after sampling.

7. Drain the sample, which shall be at a temperature not above 70°F, into a clean casserole and add 10 drops of starch indicator solution.

8. Titrate with 0.1N $Na_2S_2O_3$ to the disappearance of the blue, starch iodine color, rinsing the tip of the buret in the sample after each addition as the end point approaches.
   CAUTION: Titration should be completed within 30 minutes after sampling.

E. CALCULATIONS

Calculate the dissolved oxygen content of the sample, in parts per million, as follows:

$$\text{Dissolved oxygen, ppm} = \frac{8000\ NS}{V}$$

E. CALCULATIONS

Where:

N = normality of the $Na_2S_2O_3$ solution

S = ml of $Na_2S_2O_3$ solution required for titration

V = ml of sample used.

OFF-GAS DETERMINATION

Method No. WC-9

A. SUMMARY OF METHOD

In the analysis of a gaseous mixture by absorption and oxidation methods, the components of the mixture are determined by a systematic measurement of changes in gas volume using the Burrell equipment. These volume changes are affected by the successive removal of certain components from the mixture by treatment with absorbing reagents and by subjecting the combustible components to oxidation. Carbon dioxide is absorbed in Disorbent (Potassium Hydroxide). Oxygen is absorbed in Oxsorbent (Chromous Chloride). Hydrogen is oxidized by passing through heated copper oxide. Nitrogen is determined by difference after all other components have been removed.

B. BURRELL SETUP PROCEDURE

1. Fill the burette and gas reservoir with aqueous salt solution. Add enough to the leveling bottle so that the burette may be filled completely and still have salt solution remaining in the leveling bottle. Add drop of phenol red for visual aid.

2. Fill the pipettes by opening the pipette to the atmosphere through the manifold. Remove the rubber stopper and gas bags, then pour the solution into the rear compartment.

B. BURRELL SETUP PROCEDURE (Cont'd)

Close the manifold stopcock, inflate the bag a little and replace the stopper. The first pipette is for the determination of carbon dioxide and is filled with Di-sorbent solution. The second pipette is for illuminants and is filled with Lusorbent. The third pipette is for oxygen and is filled with Oxsorbent.

NOTE: Oxsorbent takes up oxygen very rapidly. It is necessary to first fill the pipette and partially fill the expansion bag with an oxygen-free gas. Direct a stream of the gas upon the Oxsorbent as it is being poured into the pipette and immediately replace the stopper and expansion bag.

3. Next bring the liquid in each pipette up to within 1/8 inch below the stopcock by opening each pipette in turn to the burette and carefully lowering the leveling bottle.

4. To test the apparatus for leaks lower the burette leveling bottle and draw in about 100 ml of air and open the burette to the manifold. Turn the end stopcock on the manifold to seal and raise the leveling bulb to the top of the support rod. A leak in any stopcock or rubber connection is indicated by the liquid rising in the burette. Drop the gas reservoirs and note whether upon standing

B. BURRELL SETUP PROCEDURE (Cont'd)

the liquid drops in any of the pipettes, indicating a leak in the rubber connections.

5. Electric Heaters

The first operation is to stabilize the copper oxide and catalyst heaters at the proper temperature. Plug in the Perma-Therm heaters and in 10-20 minutes they will be ready.

6. Filling Capillaries with Nitrogen

a. The manifold, copper oxide, and catalyst tubes should be filled with nitrogen before the analysis is started.

b. To prepare the nitrogen, draw about 30 ml of pure air into the burette and remove the oxygen by passing the air into the oxorbent until no further absorption takes place.

c. After sweeping the manifold and tubes with nitrogen, open the oxidation tubes to the manifold.

d. Establish the nitrogen therein at atmospheric pressure by leveling the confining liquid in the leveling bottle and burette.

e. When level, close the oxidation tubes and manifold and discharge the nitrogen from the burette.

B. BURRELL SETUP PROCEDURE (Cont'd)

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e. When level, close the oxidation tubes and manifold and discharge the nitrogen from the burette.

B. BURRELL SETUP PROCEDURE (Cont'd)

7. Volume of Sample

a. In general, the best procedure is to take as large a sample as may be conveniently handled throughout the various stages of the analysis. Errors will be of less magnitude than if a small sample is used. With a 100 ml sample, the volume of each component determined is equal to the percentage of that component.

b. When aqueous salt solution is used as the confining liquid, a little more than 100 ml of the sample is drawn into the burette. The burette stopcock is closed and the sample is allowed to stand for one minute to permit the confining liquid to drain down the sides of the burette. The leveling bottle is elevated above the confining liquid in the burette until the liquid level in the burette is exactly 100, thus placing the gas under a slight positive pressure. The connecting tubing is then pinched securely between the thumb and forefinger and the burette stopcock opening to the atmosphere momentarily, thus bringing the 100 ml of gas in the burette to atmospheric pressure. When aqueous salt solution is used as the confining liquid, the sample should be allowed to stand in the burette for one minute prior to each reading. This insures a uniform time for drainage down the side of the burette.

C. PROCEDURE

Carbon Dioxide by Absorption

1. Raise the burette leveling bottle slightly, thus putting the gas in the burette under slight pressure. This prevents any liquid from the pipette being pulled into the manifold.

2. Then turn the manifold stopcock to connect to the pipette and continue raising the burette leveling bottle until the confining fluid reaches the top of the burette and all the gas has been passed into the pipette.

3. Lower the burette leveling bottle bringing the gas back into the burette.

4. Repeat Steps C-2 and C-3.

5. The last time the gas is returned to the burette, bring the level of the potassium hydroxide solution to the reference point on the capillary stem of the pipette.

6. Close the pipette stopcock and read the burette.

7. The gas should be passed twice more into the potassium hydroxide pipette as a check. If the reading is the same as before, all of the carbon dioxide has been removed and the operator may proceed with the analysis. If more than six passes are required to get complete absorption, the solution should be changed.

C. PROCEDURE (Cont'd)

8. The volume after absorption of carbon dioxide subtract from the initial volume of sample equals the volume of carbon dioxide.

Oxygen by Absorption

9. Next pass the gas twice into the pipette containing chromous chloride and read the burette.

10. Pass the gas once more to make sure that all the oxygen has been removed and read the burette.

11. The volume after absorption of oxygen subtracted from the volume after absorption of carbon dioxide is equal to the volume of oxygen in the sample.

Hydrogen by Oxidation with Copper Oxide

12. Place the leveling bottle on the top of the platform and regulate the flow of gas by means of the burette stopcock.

13. Permit the gas to flow through the copper oxide tube at about 10 ml per minute.

14. When all the gas has passed through the copper oxide tube, draw the gas back into the burette by way of the copper oxide tube at the same flow rate.

C. PROCEDURE (Cont'd)

15. Four such double passes through the copper oxide tube generally suffice to completely oxidize the hydrogen.

16. If a high concentration of hydrogen exists additional passes may be necessary.

17. Continue passes until two identical readings are obtained.

18. Draw the sample back into the burette through the copper oxide tube and read the burette.

19. Any contraction in volume is due to the oxidation of hydrogen and is equal to the volume of hydrogen in the sample.

Nitrogen

1. Any gas remaining in the burette at this stage is due to the nitrogen in the sample.

NOTE: At the completion of the analysis, before permitting the heater to cool, open the copper oxide tube to the atmosphere through the manifold and also close the reservoir stopcock.

CAUTION:

1. Errors may be introduced by the reagents becoming exhausted.

C. PROCEDURE (Cont'd)

The operator, by check analysis and by keeping a record of the amount of gas a reagent has absorbed, may avoid this possibility.

2. Incomplete absorption caused by insufficient contact with the reagent may be eliminated by repeating passes until constant readings are obtained.

3. The solutions must not be allowed to pass into the main manifold header. Wash out the header periodically with acidulated water even though it has not been apparent that any solution has entered.

4. Keep stopcocks (Silicon type) greased to avoid leaks and be sure that all rubber connections are sound.

5. Before making a final analysis of a gas that differs appreciably in composition from the gas previously analyzed, pass a sample through the solution in the regular manner in order to bring the solutions into equilibrium with the new sample.

6. Radioactive gases should be vented to exhaust and analyze under a fume hood or equivalent.

CHROMATE DETERMINATION

Method No. WC-10

A. SUMMARY OF METHOD

When potassium iodide solution is added to an acidified water sample containing hexavalent chromium (chromates), free iodine is released in proportion to the chromate originally present. The amount of iodine is determined by titration with standard sodium thiosulfate. Starch solution is used as the indicator since it produces a blue starch iodine complex in the presence of free iodine. The end point of the titration is marked by the disappearance of this blue color which is an indication that all the free iodine has been consumed. Sodium acetate and EDTA are added before the titration to complex interferences and prevent them from reacting.

B. APPARATUS

1. Burette - 10 ml size (Presto-Fil Burette Assembly could be used.)

2. Porcelain Casserole - 140 ml capacity.

3. Graduated Cylinder - 50 ml.

4. Dropping bottles - two 2-ounce size.

5. Normal laboratory glassware is required for this work.

CHROMATE DETERMINATION

C. REAGENTS AND MATERIALS

1. Purity of Reagents - Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in standardization of these reagents shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D1193).

3. 0.01N Sodium Thiosulfate Solution - This standard solution can be purchased from Fisher Scientific Company.

4. Hydrochloric Acid Solution - Measure 100 ml of concentrated (12.1N) hydrochloric acid and add 100 ml of water.

5. Sodium Acetate Powder - Fisher Chemical Cat. #S-209.

6. Ethylenediamine Tetroacetic Acid - Fisher Chemical Cat. #E-478.

7. Concentrated Potassium Iodide - This solution can be purchased from Fisher Scientific Company. Excess solid should be present.

CHROMATE DETERMINATION

C. REAGENTS AND MATERIALS (Cont'd)

8. Starch Indicator Solution - Fisher Chemical Cat. #So-S-408.

D. PROCEDURE

1. Measure 50 ml of filtered sample in a graduate and pour into casserole.

2. Stir while adding 5 ml of 1:1 hydrochloric acid and 10 drops of concentrated potassium iodide solution.

NOTE: Allow the solution to set for 2 minutes. The solution will turn to a color which may vary from amber to rust red, depending upon the chromate concentration present in the sample.

3. Add approximately 5 gms of sodium acetate powdered and approximately 0.2 gm EDTA (see step C-6).

4. Stir for one or two minutes. Allow the solution to set for 5 minutes.

5. Start titrating solution in casserole with 0.01N sodium thiosulfate until the color weakens to a straw yellow color.

6. Stop titrating at this point and add 10 drops of starch indicator. The solution will then turn a deep blue or blue-black.

D. PROCEDURE (Cont'd)

7. Resume the titration, adding 0.01N sodium thiosulfate dropwise until the absence of the starch-iodine blue color.

NOTE: The specific color of the endpoint may vary depending upon what other substances are present in the sample. Hence, the solution should be titrated to the absence of the starch-iodine blue color and not to a colorless endpoint.

8. To check the endpoint, add another 5 drops each 1:1 hydrochloric acid and potassium iodide solution. If no blue color reappears, the burette reading is used in the calculation. However, if a color change does occur, continue titrating as in step D-6.

E. CALCULATIONS

Burette reading in (ml) per 50 ml sample X 7.7 = ppm of chromate as chromate (CrO_4).

NOTE: The burette reading in ml, per 50 ml sample:

a.) X 10.8 = ppm chromate as sodium chromate (Na_2CrO_4).

b.) X 0.63 = grains per gallon of chromate as sodium chromate (Na_2CrO_4).

c.) X 7.7 = ppm of chromate as chromate (CrO_4).

BORON DETERMINATION

Method No. WC-11A

A. SUMMARY OF METHOD

In the presence of boron, a solution of carmine or carminic acid in concentrated sulfuric acid changes from bright red to a bluish red or blue, depending on the concentration of Boron present. The ions commonly found in water do not interfere with this method. Samples should be stored in polyethylene bottles or in boron-free glassware. The transmittance of the colored solution is measured with the DU Spectrophotometer using a 1 cm cell at a wavelength of 585 mμ.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Spectrophotometer - Beckman DU Spectrophotometer is preferred.

3. Pipetts - 1, 2, 5 and 10 ml capacity is needed.

4. Flask - six each 100 ml and 50 ml volumetric flasks.

C. REAGENTS AND MATERIALS

1. Purity of Reagents - Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee

C. REAGENTS AND MATERIALS (Cont'd)

on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used preparing the reagents and in standardization of these reagents shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D1193).

3. Standard Boric Acid Solution - Dissolve 0.5717 grams of boric acid crystals in water and dilute to 1000 ml. (1.00 ml equals 0.100 mg Boron).

CAUTION: Since boric acid crystals lose weight on drying at 105° C, a reagent meeting step C-1 specifications should be used and kept tightly stoppered to prevent absorption of air moisture.

4. 12.1N Hydrochloric Acid - Concentrated hydrochloric acid (HCl).

5. 36.0 N Sulfuric Acid - Concentrated sulfuric acid (H_2SO_4).

6. Carmine Solution - Dissolve 0.92 grams of carmine N.F. 40, or carminic acid in 1 liter of H_2SO_4.

BORON DETERMINATION

D. PROCEDURE

1. Pipet 1.0, 2.0, 5.0 and 10.0 ml of the standard boric acid solution into separate 100 ml volumetric flasks. Also prepare a blank with no boric acid standard added.

NOTE: The boric acid solution aliquots represents boron concentrations of 1, 2, 5 and 10 ppm respectively.

2. Dilute to 100 ml with water.

3. Measure 2 ml of each solution and transfer each into clean dry 50 ml volumetric flasks.

4. Add two drops of concentrated hydrochloric acid (HCl).

5. Pipet 10 ml of concentrated sulfuric acid (H_2SO_4) into each flask.

NOTE: Allow sufficient time for drainage of sulfuric acid (H_2SO_4) from the side walls of the flasks.

6. Swirl the solution with caution and allow solutions to cool to room temperature.

7. Pipet 10 ml of carminic acid solution into each flask. Stopper and shake for 1 or 2 minutes.

CAUTION: Incomplete mixing in this step can cause bubbles to be present when transferred to the DU-Cells. (This can be a serious source of error.)

D. PROCEDURE (Cont'd)

8. Allow the solutions to stand for 1 hour and read the transmittance on the DU-Spectrophotometer.

9. Secure a fresh sample (needed to be analyzed for boron content) and pipet 2 ml of the 100 ml sample into a clean dry 50 ml volumetric flask.

10. Repeat steps D-4, D-5, D-6, D-7 and D-8.

NOTE: Carry a reagent blank throughout the entire procedure.

11. Read boron concentration in ppm from the standard curve mentioned in step E-1.

E. CALCULATIONS

1. Plot transmittance versus ppm on semi-log paper from readings obtained from steps D-8.

CAUTION: Since the carmine reagent deteriorates the standard curve should be checked daily.

BORON DETERMINATION

Method No. WC-11B

A. SUMMARY OF METHOD

The concentration of Boron in Sodium Pentaborate Decahydrate can be determined by using a hydrometer to measure the specific gravity.

B. APPARATUS

1. Normal laboratory glassware is required for this method.

2. Hydrometer - To be able to read between 1.000 thru 1.100 specific gravity range.

3. Thermometer - To be able to read temperature between 0-212°F.

4. Graduated Cylinder - 1000 ml

5. Hot plate or water bath.

C. REAGENTS AND MATERIALS

None

D. PROCEDURE

1. Collect a sample of the Sodium Pentaborate Decahydrate solution in the 1000 ml graduated cylinder.

2. Maintain the temperature of the sample at 80 F by means of a hot plate or water bath.

D. PROCEDURE (Cont'd)

3. Place the hydrometer in the sample and record the specific gravity.

4. Determine the concentration (w/o) of Sodium Pentaborate Decahydrate from WC-11-1, which plots the relationship of concentration versus specific gravity of Sodium Pentaborate Decahydrate at 80 F.

E. CALCULATIONS

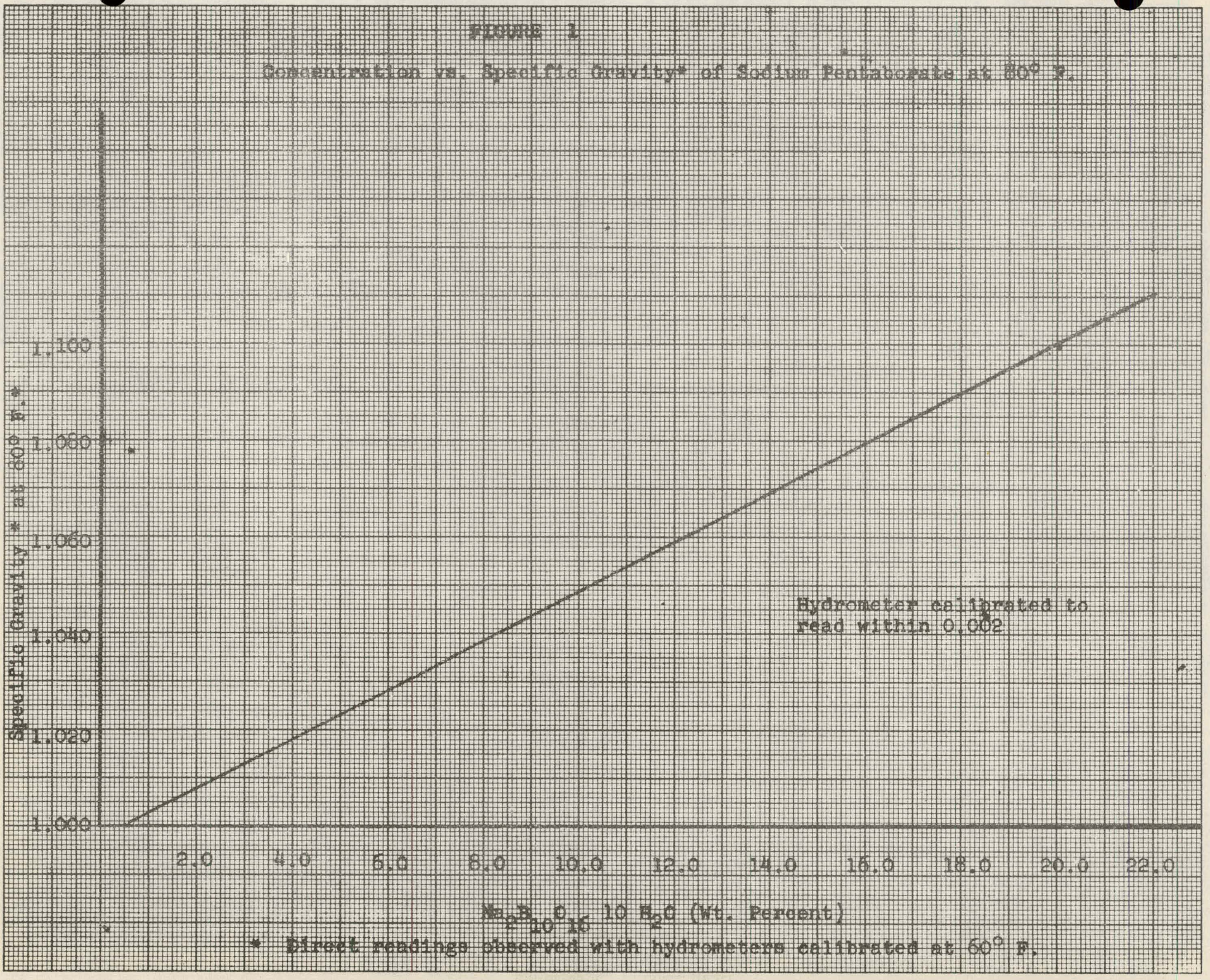
Convert the concentration (w/o) determined in step D-4 as follows:

$$\text{Boron}^{\text{natural}}\ (\text{ppm}) = (\text{w/o})(10^4)\ (0.183)$$

$$\text{Boron}^{10}\ (\text{ppm}) = \text{ppm Boron}^{\text{natural}} \times (0.1960)$$

FIGURE 1

Concentration vs. Specific Gravity* of Sodium Pentaborate at 60° F.



* Direct readings observed with hydrometers calibrated at 60° F.

COPPER DETERMINATION

Method No. WC-12

A. SUMMARY OF METHOD

This method is based on the measurement of the intensity of the yellow color of the cuprous complex of 2-9 dimethyl - 1, 10 - phenanthroline (neo-cuproine). Full development of the color takes place over the p^H range from 2.3 to 9.0. However a buffer phase is used to produce an aqueous phase with a p^H of 4.0 to 6.0. The copper is reduced with hydroxylamine hydrochloride and the p^H of the solution is adjusted with a sodium citrate solution. The cuprous ion is then reacted with neo- cuproine and the yellow complex extracted with chloroform. The method follows Beer's Law up to a concentration of 5 ppm Cu. The transmittance is measured at 437 mμ on the DU spectrophotometer using a 10 cm cell.

B. APPARATUS

1. Spectrophotometer - Beckman DU Spectrophotometer is preferred.

2. Normal laboratory glassware is required for this work.

3. 2 each - 10 cm cell.

4. 12 each - 125 ml Squibb separatory funnels.

B. APPARATUS (Cont'd)

5. 12 each - 100 ml volumetric flasks

6. 12 each - 250 ml beakers

C. REAGENTS AND MATERIALS

1. Purity of Reagents - Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in standardization of these reagents shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D1193).

3. 14.8N Ammonium Hydroxide - Concentrated ammonium hydroxide (NH_4OH).

4. Copper, Standard Soltuion (1 ml = 0.02 mg Cu.) Weigh 0.200 gram of electrolytic copper. Place it in a 250 ml beaker under a hood, add 3 ml of water and 3 ml of HNO_3 and cover the beaker with a watch glass. After the metal has completely dissolved

C. REAGENTS AND MATERIALS (Cont'd)

add 1 ml of H_2SO_4 (sp.gr. 1.84) and heat on a hot plate just short of complete dryness. DO NOT bake the residue. Cool the residue, wash down the sides of the beaker and the bottom of the watch glass, and again evaporate the solution nearly to dryness to expel the HNO_3. Cool the residue, dissolve it in water, and dilute the solution to 1 liter. Make the standard as needed by diluting 100 ml of the prepared solution to 1 liter with water. One milliliter of the standard contains 0.02 mg Cu or when diluted to 50 ml with water it represents a 0.4 ppm Cu solution.

5. 12.1N Hydrochloric Acid - Concentrated hydrochloric acid (HCl).

6. Hydroxylamine Hydrochloride Solution - (200 g/l) - Dissolve 40 grams of hydroxylamine hydrochloride (NH_2OH HCl) in water and dilute to 200 ml.

7. Neocuproine Solution (1 g/l) - Dissolve 0.1 gram of neocuproine (2, 9 - dimethyl - 1, 10 - pheonthroline) in 50 ml of isopropyl alcohol. Dilute the solution to 100 ml with water.

8. 15.7N Nitric Acid - Concentrated nitric acid (HNO_3).

COPPER DETERMINATION

C. REAGENTS AND MATERIALS (Cont'd)

9. Sodium Citrate Solution (250 g/l) - Dissolve 250 grams of hydrated sodium citrate ($Na_3C_5H_7O$) in water and dilute to 1 liter. Add 10 ml of $NH_2OH.HCl$ solution and 10 ml of neocuproine solution. Extract copper impurities in the solution with 50 ml of $CH\ Cl_3$, discarding the chloroform layer.

10. 36N Sulfuric Acid - Concentrated sulfuric acid (H_2SO_4)

11. Isopropyl Alcohol

12. Chloroform ($CHCl_3$).

D. PROCEDURE

1. Prepare a series of standard copper solutions by pipetting 1, 2, 5, 10 ml aliquots into 125 ml Squibb separatory funnels. Also prepare a blank with no copper standard added. Add 0.1 ml of hydrochloric acid (HCl) and dilute to 50 ml with water.

2. Add 5 ml of Hydroxylamine Hydrochloride $NH_2OH.HCl$ solution and shake for 30 seconds.

3. Add 10 ml of sodium citrate solution and shake for 30 seconds.

COPPER DETERMINATION

D. PROCEDURE (Cont'd)

4. Add 10 ml of neocuproine solution and shake for 30 seconds.

5. Add 30 ml of chloroform and shake vigorously for 30 seconds.

6. Allow the funnel to stand 5 minutes to permit aqueous and chloroform layers to separate.

7. Drain the chloroform layer into a dry flask and repeat step D-5 with 20 ml of chloroform.

8. Combine the chloroform extracts in a volumetric flask and dilute to 50 ml with isopropyl alcohol.

9. Read the per cent transmittance on the DU Spectrophotometer at 437 mμ using 10 cm cells.

10. Secure a fresh sample (sample needed to be analyzed for copper content) and pipet a 50 ml aliquot of the acidified sample into a 125 ml Squibb separatory funnel.

11. Repeat steps D-2, D-3, D-4, D-5, D-6, D-7 and D-8.

12. Repeat step D-9 and obtain copper concentration from curve produced on step E-1.

D. PROCEDURE (Cont'd)

CAUTION: If the water contains interfering substances such as organic matter, sulfide, or chromium (when ratio of Cr to Cu is 5 to 1), the following preliminary sample treatment is required:

13. Transfer 100 ml of the acidified sample to a 250 ml beaker.

14. Add 1 ml of Sulfuric Acid H_2SO_4 and 5 ml of Nitric Acid HNO_3.

15. Evaporate in a fume hood to dense white sulfur trioxide fumes carefully on a hot plate.

16. If solution remains colored repeat the treatment with an additional 5 ml of Nitric Acid HNO_3.

17. If organic matter is difficult to destroy, repeat the treatment with 5 ml of HNO_3 and 5 ml of hydrogen peroxide (H_2O_2).

18. Evaporate the solution to complete dryness.

19. Rinse the sides of the beaker and watch glass with water.

20. Evaporate to dryness again and expel all Nitric Acid HNO_3.

COPPER DETERMINATION

D. PROCEDURE (Cont'd)

21. Add about 80 ml of water to the residue, bring to a boil, cool, and if turbid, filter.

22. Adjust the p^H to 4 to 6 by dropwise addition of NH_4OH using range p^H paper.

23. Add 0.2 ml of hydrochloric acid (HCl) and dilute to 100 ml in a volumetric flask with demineralized water.

24. Pipet a 50 ml aliquot into a 125 ml Squibb separatory funnel.

25. Repeat steps D-11 and D-12.

E. CALCULATIONS

1. Plot the reading from step D-9 versus concentration of copper on semi-log paper.

HARDNESS DETERMINATION

Method No. WC-13

A. SUMMARY OF METHOD

Hardness in water is caused principally by the elements calcium and magnesium and sometimes by iron and aluminum. Total hardness is determined by titration at p^H 10.0 with a standardized solution of the disodium salt of ethylenediamine tetraacetic acid (Versene). Eriochrome Black T is used as the indicator. Magnesium reacts with the indicator to form a wine-red complex. Calcium is completely converted to a colorless complex by the titrating solution before the magnesium is removed from its complex with the indicator. The end point is reached when the blue color of the indicator is visible with no trace of the wine-red color of the magnesium complex. Since calcium will not cause a color change with the indicator, magnesium is added to the titrating solution to insure formation of the wine-red color when titrating samples containing calcium but no magnesium. The interference of copper and iron, up to 10 ppm is eliminated by the addition of sodium sulfide.

B. APPARATUS

1. Normal laboratory glassware is required for this work.
2. Microburet
3. Desiccator - The desiccator must hold four 1 inch diameter samples similar to Fisher No. 8-615.

B. APPARATUS (Cont'd)

4. Oven - Oven should be gravity convection type and be able to supply uniform heat at 110° C to a ± 0.5° C. (Fisher No. 13-244-1 or equivalent).

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D 1193).

3. Buffer Solution - Add 67.5 g of Ammonium Chloride (NH_4Cl) in 380 ml of water. Add 570 milliliters of concentrated Ammonium Hydroxide.

4. Sodium Sulfide Solution - Dissolve 45 grams of sodium sulfide ($Na_2S \cdot 9H_2O$) in 100 milliliters of water.

5. Eriochrome Black T Indicator - Dissolve 0.025 grams of dye in 50 milliliters of water. This reagent will not keep indefinitely. Make fresh after two weeks.

C. REAGENTS AND MATERIALS (Cont'd)

6. Sodium Ethylenediamine Tetraacetate Solution - Dissolve 4.0 grams of disodium ethylenediamine tetraacetate dihydrate in approximately 800 ml of water.

7. Standard Titrating Solution - Add .1 gram of magnesium chloride ($M_gCl_2 \cdot 6H_2O$) to Sodium (Di) Ethylenediamine Tetraacetate Solution, (1 ml=1 mg Ca CO_3 Standard Solution).
CAUTION: Store solution in a plastic bottle.

8. Standard Hard Water - Oven dry several grams of calcium carbonate crystals ($CaCO_3$) at 105° C for several hours (overnight should be sufficient). Transfer to a desiccator and cool for 30 minutes. Weigh 1.00 gram of dry calcium carbonate crystals into a 500 ml erlenmeyer flask. Add (1-1) hydrochloric acid (HCl) until all the calcium carbonate ($CaCO_3$) has been dissolved. Add 200 ml of water and boil for a few minutes to expell CO_2. Cool, add a few drops of methyl red indicator and adjust to the intermediate orange color (pH 5.3) by addition of 3N ammonium hydroxide (NH_4OH) and (1-1) hydrochloric acid (HCl) as required. Transfer quantitatively to a liter volume flask and dilute to 1-liter with water.
NOTE: This standard contains 1.000 mg $CaCO_3$ in each milliliter which represents 1000 ppm.

HARDNESS DETERMINATION

D. PROCEDURE

1. Measure accurately 100 ml of sample and transfer to 250 ml erlenmeyer flask.

2. Add 1 ml of buffer solution.

3. Add 3 drops of sodium sulfide solution.

4. Add 2 drops of Eriochrome Black T Indicator and stir for 1 or 2 minutes.

5. While stirring the solution, titrate slowly (See C-7 standard solution) using a microburet.

NOTE: Titrate until the wine-red color disappears and a blue color remains.

E. CALCULATIONS

Total hardness as ppm $CaCO_3$ =

$$\frac{(\text{ml titrating solution})\ (1000)}{(\text{Volume of sample, ml})}$$

PHOSPHATE DETERMINATION

Method No. WC-14

A. SUMMARY OF METHOD

Orthophosphate reacts with ammonium molybdate in an acid medium to form a phosphomolybdate which in turn is reduced to a molybdenum blue complex with stannous chloride. This color intensity is proportional to the phosphate concentration of the sample.

B. APPARATUS

1) Spectrophotometer - Beckman DU Spectrophotometer is preferred.
2) Normal laboratory glassware is required for this work.

C. REAGENTS AND MATERIALS

1) Purity of Reagents - Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2) Purity of Water - All water used in preparing the reagents and in standardization of these reagents shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D1193).

PHOSPHATE DETERMINATION

C. REAGENTS AND MATERIALS (CONT'D)

3) Phosphate, Standard Solution (1 ml=0.1 mgPO_4). Dissolve 0.1433 g of oven-dried potassium dihydrogen phosphate (KH_2PO_4) in water and dilute to 1 liter in a volumetric flask.

4) Ammonium Molybdate Solution

Dissolve 25 gms of ammonium molybdate in about 800 ml of water and dilute to 1-liter with water.

5) Sulfuric Acid Solution

Add 310 ml of concentrated sulfuric acid (H_2SO_4) to about 600 ml of water. Cool and dilute to 1-liter with water.

6) Stannous Chloride Solution

Dissolve 2.5 gms of stannous chloride ($SnCl_2$-$2H_2O$) in 10 ml of concentrated hydrochloric acid (HCl) and dilute to 100 ml with water.

CAUTION: Filter if turbid. Add a layer of pure mineral oil 5 mm thick over the surface of the solution to minimize oxidation.

NOTE: The reagent can also be preserved several weeks by adding mossy tin and storing in a refrigerator.

PHOSPHATE DETERMINATION

D. PROCEDURE

1) Prepare a series of standard phosphate solutions to cover the range from 0 to 25 ppm. Prepare the standards by diluting suitable volumes of phosphate solution (1 ml - 0.1 mg PO_4) to 50 ml with water. One milliliter of phosphate solution (1 ml - 0.1 mg PO_4) diluted to 50 ml with water produces a standard containing 2.0 ppm of phosphate.

2) Add 4 ml of sulfuric acid solution (H_2SO_4) to each sample and mix.

3) Add 4 ml of ammonium molybdate solution to each sample and mix.

4) Add 10 drops of stannous chloride solution to each sample and mix for 1 or 2 minutes.

5) Allow exactly 10 minutes for color development.

6) Measure the absorbance at 650 mμ with a spectrophotometer, using water as the reference sample. Plot the absorbance values obtained as ordinates and the corresponding phosphate concentrations as abscissas.

7) Transfer 50 ml of clear sample into an Erlenmeyer flask.
NOTE: Filter with suction if suspended matter is present into an Erlenmeyer flask. If the sample contains more than 25 ppm PO_4, use a correspondingly smaller sample.

D. PROCEDURE (Cont'd)

8) Repeat steps D-2 through D-6.

E. CALCULATIONS

Calculate the concentration of phosphate, in parts per million, as follows:

$$\text{Phosphate, ppm} = C \frac{50}{S}$$

where:

C = parts per million phosphate ion indicated by the calibration curve for the determined color absorbance, and

S = milliliters of sample.

SULFATE DETERMINATION

Method No. WC-15

A. SUMMARY OF METHOD

Sulfate ion is precipitated and weighed as barium sulfate after removal of silica and other insoluble matter. This method is applicable to samples containing approximately 20 to 100 ppm of sulfate ion (So_4^{--}). It can be extended to higher or lower ranges by adjusting the sample size.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Desiccator - The desiccator must hold four porcelain crucibles similar to Fisher No. 8-615.

3. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

4. Muffle Furnace - To be able to hold four crucibles and also designed for continuous operation at temperatures up to 900°C (1650°F).

5. The following laboratory supplies are needed:

   a. Porcelain crucible

   b. Hot plate

SULFATE DETERMINATION

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the specification for Reagent Water (ASTM Designation D 1193).

3. 14.8N Ammonium Hydroxide - Concentrated ammonium hydroxide (NH_4OH).

4. Barium Chloride Solution - Dissolve 118 g of barium chloride ($Ba\ Cl_2 \cdot 2H_2O$) in water and dilute to 1 liter.

5. (1-9) Hydrochloric Acid - Mix 1 volume of concentrated hydrochloric acid (HCl) with 9 volumes of water.

6. (48%) Hydrofluoric Acid - Concentrated hydrofluoric acid (HF).

7. Methyl Orange Indicator - Dissolve 0.05 gm of methyl orange in 100 ml of water.

8. 15.7N Nitric Acid - Concentrated nitric acid (HNO_3).

SULFATE DETERMINATION

C. REAGENTS AND MATERIALS (Cont'd)

9. Picric Acid - Saturated aqueous solution.

10. Silver Nitrate Solution - Dissolve 10 gm of silver nitrate ($AgNO_3$) in water and dilute to 100 ml.

11. 36N Sulfuric Acid - Concentrated sulfuric acid (H_2SO_4).

D. PROCEDURE

1. Filter the sample using a fine filter paper.

2. Measure into a clean beaker a quantity of the clear filter sample containing sulfate ion equivalent to 10 to 50 mg of barium sulfate ($BaSo_4$).

NOTE: Adjust the volume by evaporation or dilution with water to approximately 200 ml.

3. Add a few drops of methyl orange and adjust the acidity of the sample by adding (1-9) hydrochloric acid (HCl) until the red end-point is reached.

4. Add 10 ml of (1-9) hydrochloric acid HCl in excess.

5. Add 10 ml of saturated picric acid solution and boil the sample for 5 minutes.

NOTE: Faster precipitation and a coarse precipitate is obtained when using saturated picric acid.

D. PROCEDURE (Cont'd)

6. After boiling the sample for 6 minutes slowly add 5 ml of hot barium chloride ($BaCl_2$) solution.

NOTE: Stir the sample vigorously while adding the ($BaCl_2$) solution.

CAUTION: Keep the temperature just below boiling until the liquid has become clear and the precipitate has settled out completely.

7. Filter the suspension of barium sulfate ($BaSO_4$) on a fine, ashless filter paper, and wash the precipitate with hot water until the washings are substantially free of chlorides, as indicated by testing the last portion of the washings with $AgNO_3$ solution.

NOTE: Discontinue washing when no more than a faint opalescence is produced in the test.

8. Place the filter paper and contents in a tared porcelain crucible.

9. Place the crucible on the door of the muffle furnace, char and consume the paper slowly without flaming.

10. Ignite the residue at 800°C for 1 hour, or until it is apparent that all carbon has been consumed.

SULFATE DETERMINATION

D. PROCEDURE (Cont'd)

11. Cool and add a drop of concentrated sulfuric acid (H_2SO_4) and a few drops of hydrofluoric acid (HF).

12. Place on a hot plate and evaporate under a hood to expel silica as silicon tetrafluoride (SiF_4).

13. Reignite at 800°C.

14. Cool in a desiccator and weigh the crucible and precipitate ($BaSO_4$) on an analytical balance to the nearest 0.1 mg.

E. CALCULATIONS

1. Calculate the concentration of sulfate ion (SO_4^{--}) in parts per million, as follows:

$$\text{sulfate } (SO_4^{--}) \text{ ppm} = \frac{(W)\ (411{,}500)}{S}$$

Where:

W = grams of $BaSO_4$

S = milliliters of sample

SILICA DETERMINATION

Method No. WC-16

A. SUMMARY OF METHOD

This method covers the determination of soluble silica in the range from 50 to 1000 ppb. This method is based on the reaction of soluble silica with molybdate ion to form a greenish-yellow complex which in turn is converted to a blue complex by reduction with 1-amino-2-napthol-4-sulfonic acid. Phosphate interference is eliminated by the use of oxalic acid. Iron, if present in large amounts, also interferes. The concentration of silica is determined by measuring the transmittance on the DU Spectrophotometer at a wavelength of 815 mμ using 1 cm cells.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Spectrophotometer-Beckman DU Spectrophotometer is preferred.

C. REAGENTS AND MATERIALS

1. Purity of Reagents - Reagent grade chemicals shall be used to prepared reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

SILICA DETERMINATION

C. REAGENTS AND MATERIALS

CAUTION: All reagents should be stored in polyethylene bottles.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D 1193).

3. Amino-Napthol-Sulfonic Acid - Dissolve 0.5 grams of 1-amino-2-Napthol-4-sulfonic acid in 50 ml of a solution containing 1 gram of sodium sulfite (Na_2SO_3). After dissolving, add the solution to 100 ml of a solution containing 30 grams of sodium hydrogen sulfite ($NaHSO_3$). Make up to 200 ml with demineralized water and store in a dark, plastic bottle. CAUTION: Prepare a fresh solution every two weeks.

4. Ammonium Molybdate Solution (100 g/l.) - Dissolve 10 grams of ammonium paramolybdate $(NH_4)_6\ Mo_7O_{24} - 4H_2O$ in 100 ml of water.

5. Hydrochloric Acid (1:1) - Mix 1 volume of concentrated HCl with 1 volume of demineralized water.

6. Oxalic Acid Solution (100 g/l) - Dissolve 10 grams of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) in 100 ml of water.

7. Silica Standard Solution (1 ml = 1 mg SiO_2) - Dissolve 4.732 grams of sodium metasilicate ($Na_2Si\ O_3 \cdot 9H_2O$) in water

C. REAGENTS AND MATERIALS (Cont'd)

and dilute to 1-liter with demineralized water. Check the concentration of this solution gravimetrically. (See appendix C) Pipette 5 ml of standard silica solution into a 1000 ml volumetric flask and dilute to mark with demineralized water. This solution contains 5 ppm SiO_2 and is used as a working solution.

D. PROCEDURE

1. From the 5 ppm working solution prepare a series of standards by pipetting aliquots of 1.0, 5.0, 10.0, and 20.0 ml into polyethylene graduated mixing cylinders. Also prepare a blank with no silica standard added.

NOTE: The silica working solution aliquots represents silica concentration of 0.05, 0.25, 0.5 and 1.0 ppm respectively.

2. Dilute each sample to the 50 ml mark.

3. Add 1 ml of (1-1) hydrochloric acid solution and 2 ml of ammonium molybdate solution, mix, allow to stand exactly 5 minutes.

4. Add 1.5 ml of oxalix acid reagent, mix well, allow to stand exactly 1 minute.

SILICA DETERMINATION

D. PROCEDURE (Cont'd)

5. Add 2 ml of amino-napthol-sulfonic acid. Mix well and allow to stand for 10 minutes for full color development.

6. Read the transmittance on the DU Spectrophotometer at 815 mμ using 1 cm cells.

7. Secure a fresh sample (sample needed to be analysed for silica content) and transfer a 50 ml sample to a polyethylene graduated cylinder.

8. Repeat steps D-3, D-4 and D-5.

9. Prepare a blank by using 50 ml of demineralized water and repeat step D-8.

10. Repeat step D-6 and obtain concentration of silica as SiO_3 directly from curve produced on step E-1.

E. CALCULATION

1. Plot percent transmittance versus ppb on semi-log paper.

NOTE: This plot should be a straight line.

CHROMIUM DETERMINATION

Method No. WC-17

A. SUMMARY OF METHOD

The sample is oxidized by acid treatment, followed by potassium permanganate treatment. A color is developed in acid solution with 1,5 diphenylcarbazide. This color (reddish-purple complex) is measured by means of a DU-spectrophotometer at 540 mμ using 1 cm cells.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Spectrophotometer - Beckman DU-Spectrophotometer is preferred.

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee of Analytical Reagents of the Amercian Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the specification for Reagent Water (ASTM Designation D 1193).

CHROMIUM DETERMINATION

C. REAGENTS AND MATERIALS (Cont'd)

3. (1-1) Ammonium Hydroxide - Mix 1 volume of concentrated ammonium hydroxide (NH_4OH) with 1 volume of water.

4. 15.7N Nitric Acid - Concentrated (low chromium content) Nitric acid.

NOTE: Reagent grade nitric acid frequently may contain sufficient chromium to interfere in this method. It may be purified by distillation in all-glass equipment.

CAUTION: Such a distillation often may need to be repeated.

5. Potassium Dichromate Standard Solution (1 ml - 0.5 ppm) Dissolve 1.41 grams of potassium dischromate ($K_2Cr_2O_7$) in water and dilute to 1-liter with water. Pipet 10 ml of this solution into a 1-liter volumetric flask and dilute to the liter mark. One milliliter of this finally-diluted solution corresponds to 0.5 ppm chromium in a 10 ml sample.

6. Potassium Permanganate Solution - Dissolve 3.16 grams of potassium permanganate ($KMnO_4$) in water and dilute to 1-liter with water.

7. Diphenylcarbazide Solution - Add 4.0 grams of phthalic anhydride to 80 ml of ethanol (95 percent) and shake for 1 or 2 minutes. Add 0.5 grams of 1,5-diphenylcarbazide and dilute to 100 ml with ethanol (95 percent). Shake occasionally to dissolve the phthalic anhydride.

C. REAGENTS AND MATERIALS (Cont'd)

CAUTION: This solution is stable for about six months if stored in a cool, dark place.

NOTE: New calibration curves should be prepared at least monthly.

8. 12.1N Hydrochloric Acid - Concentrated hydrochloric acid (HCl).

9. Sodium Dihydrogen Phosphate Solution - Dissolve 138 grams of sodium dihydrogen phosphate (NaH_2PO_4) in water and dilute to 1-liter with water.

10. 36N Sulfuric Acid - Concentrated sulfuric acid (H_2SO_4).

11. (1-49) Sulfuric Acid - Mix 1 volume of concentrated sulfuric acid (H_2SO_4) cautiously and with stirring, with 49 volumes of water.

12. Wash Acid - Mix 50 ml of concentrated nitric acid with 150 ml of concentrated hydrochloric acid and add 200 ml of water.

D. PROCEDURE

CAUTION: All glassware should be rinsed in C-12 wash acid solution and then with water before use.

D. PROCEDURE (Cont'd)

1. Pipet accurately 1.0, 2.0, 3.0, 5.0, 8.0 and 10.0 ml of the diluted standard solution into six separated 125 ml Erlenmeyer flasks. Into another 125 ml Erlenmeyer flask, pipet 10 ml of water for use in preparing the reference solution.

NOTE: The chromium standard solution aliquots represent chromium concentrations of 0.05, 0.1, 0.15, 0.25 0.4 and 0.5 ppm respectively.

2. Secure a fresh sample (sample needed to be analyzed for chromium content).

NOTE: If reducing impurities are absent, hexavalent chromium may be determined directly by omitting steps D-3 through D-10. Add 13 ml of (1-49) sulfuric acid H_2SO_4 and proceed as described in step D-11. (Standard solution should proceed to step D-11).

3. Add 5 ml of concentrated nitric acid and evaporate just to dryness.

CAUTION: Do not bake.

4. Cool and add an additional 5 ml of concentrated nitric acid, followed by 2 ml of concentrated sulfuric acid H_2SO_4.

D. PROCEDURE (Cont'd)

5. Evaporate to fumes, then heat gently for 1 minute.

NOTE: If the residue is discolored by organic matter, cautiously add 2 ml of concentrated H_2SO_4 to reduce fumes, and repeat treatment as often as necessary. It may be necessary to add more concentrated sulfuric acid (H_2SO_4) to prevent the mixture from becoming dry.

6. Cool the solution and add 17 ml of water and neutralize with (1-1) ammonium hydroxide NH_4OH.

7. Add 13 ml of (1-49) sulfuric acid H_2SO_4. Swirl and, if necessary, warm to achieve solution.

8. Filter through fine filter paper and wash the filter three times with 5 ml portions of water. Filtrate and washings should be collected in a 250 ml beaker.

9. Add 12 drops of potassium permanganate ($KMnO_4$) solution. Place on a hot plate on low heat for 20 minutes. If the pink color disappears, add an additional 12 drops of potassium permanganate ($KMnO_4$)solution to maintain a slight excess.

10. Add 3 drops of concentrated hydrochloric acid and

D. PROCEDURE (Cont'd)

heat the solution until the color of the potassium permanganate ($KMnO_4$) disappears.

NOTE: If any turbidity or precipitate is present at this point, clarify by centrifuging.

11. Transfer the solution to a 50 ml volumetric flask and add 2 ml of the 1,5 diphenylcarbazide solution. Shake for 1 or 2 minutes and let stand for 1 minute.

12. Add 5.0 ml of sodium dihydrogen phosphate (NaH_2PO_4) solution and let stand at least 5 minutes but not more than 30 minutes. Dilute to the 50 ml mark and shake for 1 or 2 minutes.

13. Read the percent transmittance on the DU-Spectrophotometer at 540 mμ using 1 cm cells.

NOTE: The spectrophotometer should be balanced at 100 percent transmittance using the D-1 blank water solution.

14. The chromium concentration in ppm is read directly from the calibration curve produced on step E-1.

E. CALCULATIONS

1. Plot percent transmittance versus ppm chromium on semi-log paper from step D-13.

NICKEL DETERMINATION

Method No. WC-18

A. SUMMARY OF METHOD

This method is based on the formation of a wine-red color complex of nickel with ammoniacal diemethylglyoxime in the presence of iodine. The color is measured directly with the DU Spectrophotometer at a wavelength of 350 mμ using a 1 cm cell.

B. APPARATUS

1. Normal laboratory glassware is required for this work.
2. Spectrophotometer - Beckman DU - Spectrophotometer is preferred.

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the specification for Reagent Water (ASTM Designation D 1193).

NICKEL DETERMINATION

C. REAGENTS AND MATERIALS (Cont'd)

3. Ammonium Citrate Solution - Dissolve 500 grams of citric acid monohydrate in 675 ml of concentrated ammonium hydroxide (NH_4OH), cool, and dilute to 1-liter with water.

NOTE: Filter solution through a fine filter paper before using the solution.

4. (1-1) Ammonium Hydroxide - Mix 1 volume of concentrated ammonium hydroxide (NH_4OH) with 1 volume of water.

NOTE: Filter solution through a fine filter paper before using the solution.

5. Dimethylglyoxime Ammoniacal Solution - Dissolve 1 gram of dimethylglyoxime in 500 ml concentrated ammonium hydroxide, and diluted to 1-liter with water.

CAUTION: Prepare fresh after two weeks.

NOTE: Filter solution same as C-3 and C-4 reagents.

6. Iodine Solution (12.7 g/l) - Dissolve 6.35 grams of iodine in a solution of 75 grams of potassium iodide (KI) in 60 ml of water and dilute to 500 ml with water.

CAUTION: Store solution in a stoppered dark bottle.

7. Nickel Solution (1 ml = 0.02 mg Ni) - Dissolve 1.000 gram of nickel (99.9 per cent Ni) in 10 ml of warm concentrated nitric acid (HNO_3). Boil to expel nitrous oxide fumes and dilute to 500 ml in a volumetric flask. Dilute

NICKEL DETERMINATION

C. REAGENTS AND MATERIALS (Cont'd)

50 ml to 1000 ml in a volumetric flask, and finally dilute 50 ml of this solution to 250 ml in a volumetric flask.

D. PROCEDURE

1. From the nickel solution C-7 prepare a series of standards by pipetting aliquots of 1.0, 2.0, 5.0, 10.0 and 25.0 ml into 100 ml volumetric flasks. Also prepare a blank with no nickel standard added.

NOTE: The nickel standard solution aliquots represent nickel concentrations of 0.4, 0.8, 2.0, 4.0 and 10.0 ppm respectively. The blank represents 0.0 ppm nickel.

2. Add water to make a volume of 50 ml.

3. Add 10 ml of ammonium citrate solution and 5 ml of iodine solution to each volumetric flask.

4. Add 20 ml of ammoniacal dimethylglyoxime solution and dilute to 100 ml with water.

5. Mix well and allow to stand for 10 minutes for full color development.

6. Read the transmittance on the DU Spectrophotometer at 530 mμ using 1 cm cells.

NICKEL DETERMINATION

D. PROCEDURE

NOTE: The spectrophotometer should be balanced to 100 per cent transmittance using the D-1 blank solution.

7. Secure a fresh sample (sample needed to be analyzed for nickel content) and transfer two 50 ml portions of the the sample into separate 100 ml volumetric flasks.

8. Repeat step D-3 for both flasks.

9. To one of the flasks repeat step D-4 and D-5.

10. To the second flask add 20 ml of (1-1) ammonium hydroxide (NH_4OH) and dilute to 100 ml with water and repeat step D-5.

NOTE: Use this solution as the blank solution.

11. Repeat step D-6.

NOTE: Read D-9 solution and use D-10 solution as the blank solution.

12. The nickel concentration in ppm is read directly from the calibration curve produced on step E-1.

E. CALCULATIONS

1. Plot transmittance versus ppm nickel on semi-log paper from step D-6.

NOTE: This plot should be a straight line.

SECTION V

RADIOCHEMISTRY METHODS

This section is a collection of radiochemical procedures for determining the activity of selected radioisotopes. The method specified for each isotope was chosen on the simplicity of the chemical operations involved, the time required for completion, and the required degree of decontamination from other radioisotopes expected to be present, based on the distribution of activity released from UO_2 fuel elements to the coolant.

The manipulations and techniques of radiochemistry and analytical chemistry are similar except for the final determination. In analytical chemistry analysis the element is identified by weight of precipitate, titration or transmission or absorption of light. In a radiochemical analysis the unknown is isolated by performing a series of chemical separations that are specific for the radionuclide to assayed. Therefore the unknown in radiochemical analysis is determined by the energy and disintegration rate of its radiation.

IODINE

Method No. RC-1

A. Summary of Method

The iodine isotopes are separated from the mixed fission product mixture by oxidizing to I_2 with nitrate and extracting into carbon tetrachloride (CCl_4). The iodine is reduced to iodide and extracted into sulfurous acid solution. This oxidation and reduction is repeated once again and the iodide precipitated as palladium iodide (PdI_2) for weighing and determining total desintegradation rate of I-131 and I-133.

B. Apparatus

1) Normal laboratory glassware is required for this work.

2) Glass Fiber Filter - 1 inch diameter x 0.01 inches thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to $\pm$ 0.01 mg during filtration and drying.

3) Filter Holder - The filter holder must hold the 1 inch filters rigidly in place during filtration.

NOTE: Care should be taken to clean the holder thoroughly between filtrations to prevent cross-contamination.

4) Desiccator - The desiccator must hold four 1 inch diameter filters similar to Fisher No. 8-615.

5) Oven - Oven should be gravity convection type and be able to supply uniform heat at 110°C to a ± 0.5°C. (Fisher No. 13-244-1 or equivalent).

6) Gamma-Ray Spectrometer - a sodium iodide scintillation detector assembly connected to the appropriate amplifier and pulse height analyzer .

7) Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

8) The following additional supplies are needed:

   a) 1 each separatory funnel, 1000 ml Squibb type

   b) 2 each separatory funnel, 125 ml Squibb type

   c) 1 each 50 ml beaker

   d) 1 each 10 ml graduated cylinder

   e) 1 each, metal/plastic spatula.

C. Reagents and Materials

1) Purity of Reagents - Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2) Purity of Water - All water used in preparing the reagents and in standardization of these reagents shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D1193).

3) Ethyl Alcohol - Either CP ethyl alcohol or denatured ethyl alcohol (denatured according to formula No. 30, Regulation No. 3 and its appendix, U. S. Bureau of Internal Revenue) shall be used.

4) 2M Sodium Carbonate - Dissolve 21 gms sodium carbonate (Na_2CO_3) in 100 ml water.

   NOTE: Heat to get complete dissolution.

5) 1M Hydroxylamine Hydrochloride - Dissolve 7 gms hydroxylamine hydrochloride ($NH_2OH.HCl$) in 100 ml water.

   NOTE: Store in cool place.

6) 1N Nitric Acid (HNO_3) - Measure 64 ml of 15.7N nitric acid (HNO_3) and dilute to 1 liter with water.

7) 0.1M Palladium chloride - Dissolve 21.4 gms of palladium chloride ($PdCl_2 - 2H_2O$) and dilute to 1 liter with water.

8) Iodine Carrier 10 mg/ml - See Section II on standardization of carrier.

9) The additional chemicals are needed:

   a) Carbon Tetrachloride (CCl_4)

   b) Sulfurous Acid (H_2SO_3)

   c) Sodium nitrite ($NaNO_2$) (solid)

   d) Sodium hypochlorite (5%)

10) 15.7N Nitric Acid - Concentrated nitirc acid (HNO_3)

D. Procedure

1) To the sample of the primary coolant, add 2 ml of standardized iodine carrier.
2) Add 50 ml of 2M sodium carbonate (Na_2CO_3) and 10 ml of 5% sodium hypochlorite. Heat to boiling and cool.
   NOTE: It is not necessary to heat to boiling to get complete isotopic exchange.
3) Transfer to a 1000 ml separatory funnel and add 25 ml of carbon tetrachloride (CCl_4).
4) Acidify by dropwise addition of conc nitric acid (HNO_3).
5) Add 15 ml of 1M hydroxylamine hydrochloride (NH_2OH-HCl) and shake separatory funnel until the brown color leaves the aqueous layer. (As shown by blue color in the (CCl_4) phase)
   Caution: Relieve gas which is built up during the shaking operation (with stopper inserted in separatory funnel, turn over and open stopcock).
6) If no color appears in either phase, repeat step 4 until blue-purple color appears in the CCl_4 phase. (Shake separatory during this operation).
7) Transfer the carbon tetrachloride (CCl_4) layer to a clean 125 ml separatory flask and wash the original aqueous layer twice more with carbon tetrachloride (CCl_4) and

combine all extracts in the 125 ml separatory flask.

Note: Discard the aqueous layer as radioactive waste.

8) Add 4ml 1N nitric acid (HNO_3) to the combined carbon tetrachloride (CCl_4) washes from step D7.

9) Shake and transfer aqueous layer to a clean separatory.

10) Wash the carbon tetrachloride phase twice more with the HNO_3-H_2SO_3 as stated in step D8.

11) Repeat step D9 and combine washes from steps D9 and D10.

Note: Discard the organic (CCl_4) layer.

12) Add approximately 5 ml of carbon tetrachloride (CCl_4) to the aqueous layer and cautiously add solid sodium nitrite ($NaNO_2$) by using a spatula and shake separatory funnel until the brown color leaves the aqueous layer. (As shown by blue color in the organic (CCl_4) phase.)

Caution: Relieve gas which is built up during the shaking operation.

13) If no color appears in either phase, repeat step D12 until blue color appears in the organic phase. (Shake separatory during this operation).

14) Repeat step D7 and discard the aqueous layer.

15) Add 5 drops 1M nitric acid (HNO_3), 4 ml water and 1 ml sulfurous acid (H_2SO_3) to the combined CCl_4 layers from step D14.

16) Shake and transfer the aqueous layer to a clean 50 ml beaker.

17) Wash the carbon tetrachloride phase twice more with the same mixture as stated in step D15.

18) Repeat step D16 and combine washes from steps D16 and D17 in a clean 50 ml braker.

Note: Discard the organic (CCl_4) layer.

19) Heat the combined aqueous solution to boiling until all excess SO_2 is driven off (at least 2 minutes).

20) Add about 2 ml palladium chloride ($PdCl_2$) solution to precipitate palladium iodide (PdI_2).

21) Digest the precipitate on a hot plate for 5 minutes.

22) Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

23) Rinse the beaker with ethyl alcohol and pour the rinsings through the filter.

24) Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

25) Place the filter containing the precipitate in an oven and dry at 110° C for 10-15 minutes. Cool in a desiccator for 10 - 15 minutes.

26) Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

27) Subtract the tare weight of the filter to obtain the weight of the precipitate.

D. PROCEDURE (Cont'd)

28) Mount the filter on a suitable holder.

Note: Suitable holders are described by Overman and Clark in "Radioisotope Techniques", McGraw-Hill, 1960 .

29) With a gamma-ray spectrometer, radioassay the precipitate.

E. Calculations

Only the 8.05 day half-life I-131 and the 21 hour half-life I-133 are to be studied. Both are Beta and Gamma emitters and may be determined by selectively counting either ray. Gamma-ray counting is preferred and should be used.

1) Plot the gamma spectrum.
2) Determine the disintegration rate of the 21 hr I-133 by determining the area under the 0.53 Mev photopeak.
3) Determine the disintegration rate of the 8.05 day I-131 by determining the area under the 0.364 Mev photopeak.

Note: A minimum waiting period of 24 hours after separation should be used for determining I-131.

4) Repeat counting the sample 24 hours after purification and repeat steps E1, E2 and E3.
5) Repeat counting the sample 3 days later and repeat steps E1, E2 and E3.
6) Plot a decay curve on semilog paper of the count rate vs time on both the 0.53 Mev I-133 and 0.364 Mev I-131 photopeaks.

IODINE METHOD

E. CALCULATIONS (Cont'd)

7. The disintegration rate of Iodine 131 and 133 is calculated using the equation:

$$\text{dpm-ml} = \frac{C}{(V)(E)(F_y)}$$

Where:

C = Counts per minute for Iodine 131 and 133 each, corrected for background counts and extrapolated back to sampling time.

E = Counting efficiency

NOTE: This factor should include the fractional abundance of the gamma ray and the photopeak detection efficiency.

F_y = Fractional chemical yield for the separation.

V = Volume of sample in ml.

MANGANESE

Method No. RC-2

A. Summary of Method

Manganese is separated from the mixed fission product mixture and precipitated as manganese dioxide. The precipitate is mounted and counted with a gamma-ray spectrometer for manganese - 54 and 56. The appropriate corrections are made for chemical yield, and radioactive decay during analysis.

B. Apparatus

1) Normal laboratory glassware is required for this work.
2) Glass Fiber Filter - 1 inch diameter x 0.01 inches thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to $\pm$ 0.1 mg during filtration and drying.
3) Filter Holder - The filter holder must hold the 1 inch filters rigidly in place during filtration.
   NOTE: Care should be taken to clean the holder thoroughly between filtrations to prevent cross-contamination.
4) Desiccator - The desiccator must hold four 1 inch diameter filters similar to Fisher No. 8-615.
5) Oven - Oven should be gravity convection type and be able to supply uniform heat at 110°C to a $\pm$ 0.5°C. Fisher No. 13-244-1 or equivalent).
6) Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

7) Gamma-Ray Spectrometer - A sodium iodide scintillation detector assembly connected to the appropriate amplifier and pulse height analyzer.

8) The following additional supplies are needed:

   a) Centrifuge cones, 50 ml

   b) Pipettes, 1 ml

   c) Hot plate

   d) Erlenmeyer flask, 125 ml

   e) Graduated cylinder, 100 ml

C. Reagents and Materials

1) Purity of Reagents - Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2) Purity of Water - All water used in preparing the reagents and in standardization of these reagents shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D1193) .

3) Ethyl Alcohol - Either CP ethyl alcohol or denatured ethyl alcohol (denatured according to formula No. 30, Regulation No. 3 and its appendix, U.S. Bureau of Internal Revenue) shall be used for this method.

4) Standardized Manganese Carrier - see section on standardization of carriers.

5) Chromium Carrier (10 mg/ml) - Dissolve 2.8 gms of potassium dichromate ($K_2Cr_2O_7$) and dilute with 100 ml of water.

6) Cobalt Carrier (10 mg/ml) - Dissolve 4 gms cobalt chloride (C_0Cl_2-$6H_2O$) and dilute with 10 ml 12N hydrochloric acid and 90 ml of water.

7) Tungten Carrier (1o mg/ml) - Dissolve 1.8 gms sodium tungstate (Na_2WO_4-$2H_2O$) and diluted with 100 ml water.

8) Saturated Sodium Bromate Solution - Dissolve 40 gms of sodium bromate in 100 ml water.

9) The following additional chemicals are needed:

   1) 30% Hydrogen peroxide (H_2O_2)

   2) Diethyl ether.

D. Procedure

1) Measure 100 ml of filtered primary coolant into a 125 ml Erlenmeyer flask and add 2 ml of standardized manganese carrier and 5 drops each of 1 ml of chromium and cobalt carriers. Add 1 ml of Tungsten carrier.

2) Add 5 ml conc. (15.7N) nitric acid (HNO_3) and evaporate to approximately 5 ml on the hot plate.

3) Transfer to a centrifuge tube using as little water as possible and centrifuge for two minutes.

4) Decant the supernate from the centrifuge tube into the Erlenmeyer flask. Discard the yellow precipitate.

5) Add 2 ml of saturated sodium bromate ($NaBrO_3$) solution and boil for three minutes to precipitate manganese dioxide (MnO_2) (the precipitate will be brown).

6) Transfer to a centrifuge tube and centrifuge for two minutes. Discard the supernate as radioactive waste.

7) Wash the precipitate with approximately 10 ml of water. Centrifuge for two minutes and discard the supernate (wash water) as radioactive waste.

8) Dissolve the precipitate in 5 ml conc. (15.7N) nitric acid (HNO_3) and 5 drops of hydrogen peroxide (H_2O_2) and heat.

9) After complete dissolution, transfer the dissolved precipitate to a clean Erlenmeyer flask.

10) Repeat step D5.

11) Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

12) Rinse the Erlenmeyer flask with 20 ml water and pour the rinsings through the filter.

13) Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

14) Place the filter containing the precipitate in an oven and dry at 110°C for 20 minutes. Cool in a desiccator for

30 minutes.

15) Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

16) Subtract the tare weight of the filter to obtain the weight of the precipitate.

17) Mount the filter on a suitable holder.

NOTE: Suitable holders are described by Overman and Clark in "Radioisotopes Techniques", McGraw-Hill, 1960.

18) With a gamma-ray spectrometer, radioassay the precipitate immediately.

E. Calculation

Only the 2.6 hour half-life Mn-56 and the 314 day half-life Mn-54 are to be studied.

1) Plot the gamma spectrum

2) Determine the count rate of the 2.6 hour Mn-56 by determining the area under the 0.845 Mev photopeak.

3) Repeat counting the sample 2, 4 and 8 hours after purification and repeat steps E1 and E2.

4) Plot a decay curve on semilog paper of the count rate vs time on the 0.845 Mev Mn-56 photopeak.

5) The disintegration rate for manganese-56 is calculated using the equation:

$$\text{dpm-ml} = \frac{C}{(V)\ (E)\ \ (Fy)}$$

where:

C = Count rate of sample in counts per minute, corrected for background counter and extrapolated back to sampling time

E = Counter efficiency

V = Volume of sample in ml.

Fy = fractional chemical yield for the separation

6) Calculate the decay correction for radioactive manganese as follows:

$$A = A_o e^{-0.693\ t/T}$$

Where:

A = activity at time, t.

A_o = activity at time zero in same units as A

e = base of natural logarithms

t = elapsed time

T = half-life of isotope in same units as t.

7) Repeat counting the sample 3 days later and repeat counting the same every seven days until a 314 day slope can be established on a semilog plot.

8) Repeat step E1 and determine the count rate of the 314 day Mn-54 by determining the area under the 0.835 Mev photopeak .

9) Repeat steps E-5 and E-6.

10) Record data and calculate concentrations on form LACBWR-RC-1.

GROSS ALPHA ACTIVITY

Method No. RC-3

A. SUMMARY OF METHOD

A sample of the coolant shall be analyzed by evaporating a sample on a stainless steel planchet and counting on a proportional counter to determine gross alpha activity.

B. APPARATUS

Evaporator Feeder - To be able to evaporate large volume samples onto a planchet. (See Figure RC-3-1).

2. Infra-red lamp.

3. 1 each - 2 inch diameter stainless steel planchets.

4. Small (clean) forceps.

5. Proportional Counting system - a proportional detector connected to appropriate amplifier and scaler type system.

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

GROSS ALPHA ACTIVITY

C. REAGENTS AND MATERIALS (Cont'd)

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D1193).

3. Concentrated Nitric Acid (15.7N) (HNO_3).

D. PROCEDURE

1. Add 5 ml concentrated (15.7N) nitric acid (HNO_3) to 500 ml of primary coolant in an Evaporator Feeder (see section B-1).

2. Using an Evaporator Feeder evaporate the 500 ml from step D-1 onto a 2 inch diameter stainless steel planchet.

3. Count on the proportional flow counter.

E. CALCULATIONS

1. Count for one hour at the alpha voltage setting.

2. Correct for a one hour planchet background and calculate

μc/ml as:

$$\mu c/ml = \frac{C}{x.22 \times 10^6 (E)(V)}$$

GROSS ALPHA ACTIVITY

E. CALCULATIONS (Cont'd)

Where:

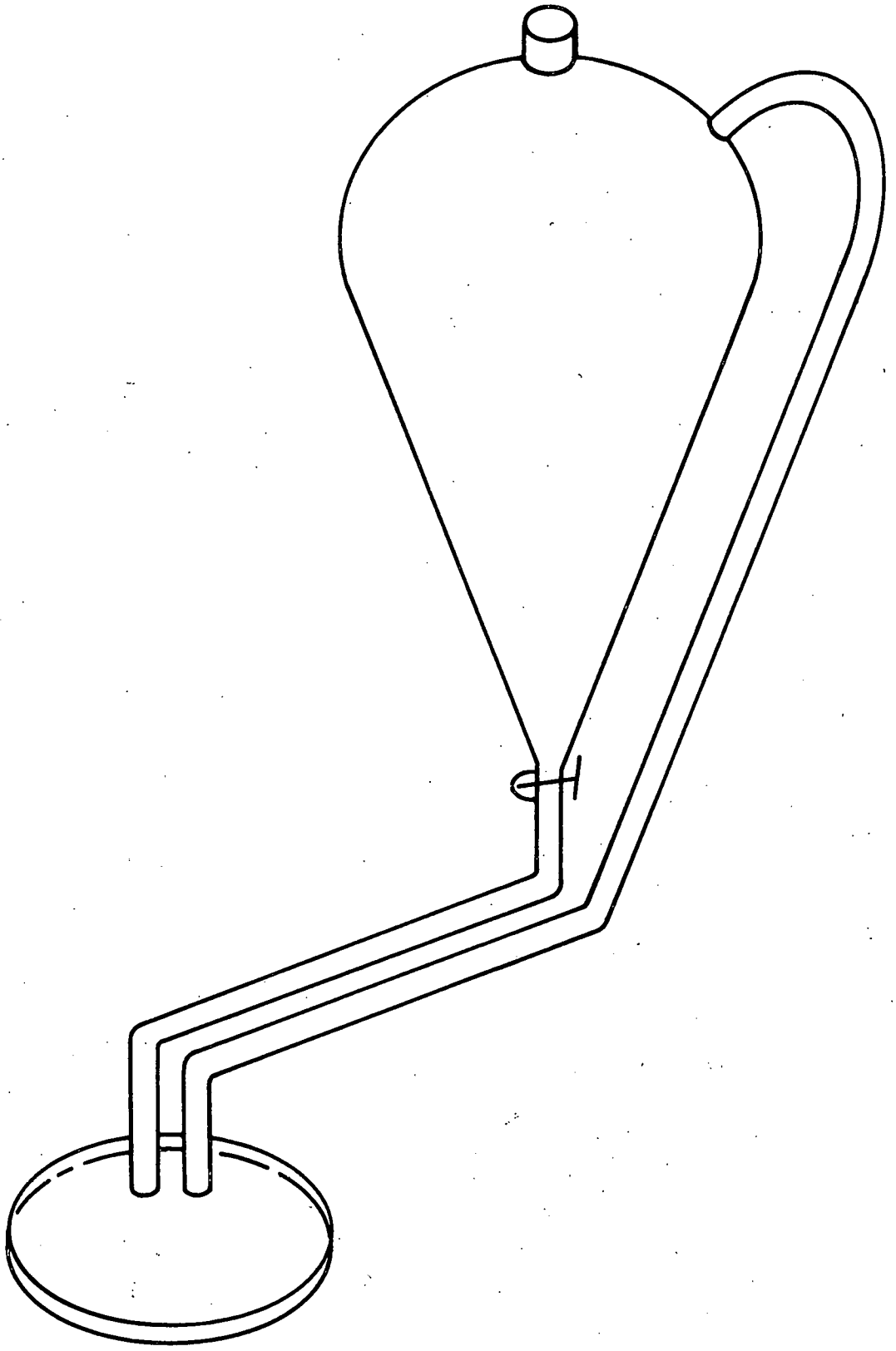
C = alpha count rate, in net counts per minute

E = counter efficiency

V = volume of original sample in ml

2.22×10^6 = conversion factor from disintegrations per minute to micro curies.

FIGURE RC-3-1



Evaporator Feeder

CESIUM METHOD

(Cesium-137, and 138)

Method No. RC-4

A. SUMMARY OF METHOD

Cesium is scavenged with iron hydroxide to remove impurities then precipitated as cesium chloroplatinate from an acid-ethyl alcohol medium. The cesium chloroplatinate is weighed and radioassayed by gamma-ray spectrometer.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Glass Fiber Filter - 1 inch diameter x 0.1 inches thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to $\pm$ 0.01 mg during filtration and drying.

3. Filter Holder - The filter holder must hold the 1 inch filters rigidly in place during filtration.

NOTE: Care should be taken to clean the holder thoroughly between filtrations to prevent cross-contamination.

4. Desiccator - The desiccator must hold four 1 inch diameter filters similar to Fisher No. 8-615.

CESIUM METHOD

B. APPARATUS (Cont'd)

5. Oven - Oven should be gravity convection type and be able to supply uniform heat at 110° C to a ± 0.5° C Fisher No. 31-244-1 or equivalent).

6. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

7. Gamma-Ray Spectrometer - A sodium iodide scintillation detector assembly connected to the appropriate amplifier and pulse height analyzer.

8. Centrifuge - A clinical centrifuge shall be used. The head should accommodate 50 ml centrifuge tubes.

9. The following additonal supplies are needed:

   a. 50 ml centrifuge tubes

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

CESIUM METHOD

C. REAGENTS AND MATERIALS (Cont'd)

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the specification for Reagent Water (ASTM Designation D 1193).

3. Cesium Carrier (10 mg/ml) - Refer to Section II on standardization of carriers.

4. Ruthenium Carrier (10 mg/ml) - Dissolve 3 grams of ruthenum chloride in 100 ml of water. Filter through a medium filter paper.

5. Zirconium Carrier (10 mg/ml) - Refer to Section II on standardization of carriers.

6. Iron Carrier (10 mg/ml) - Refer to Section II on standardization of carriers.

7. 6N Sodium Hydroxide - Dissolve 126 grams sodium hydroxide (NaOH) in 500 ml of water.

8. 6N Hydrochloric Acid - Measure 500 ml of concentrated hydrochloric acid and dilute to 1-liter.

9. Methyl Red Indicator - Dissolve 1 gram of methyl red in 600 ml of alcohol and dilute to 1-liter.

C. REAGENTS AND MATERIALS (Cont'd)

10. 10% Chloroplatinic Acid - Dissolve 10 grams chloroplatinic acid crystals ($H_2PtCl_6 \cdot 6H_2O$) in 90 ml of water.

11. Ethyl Alcohol - Either CP ethyl alcohol or denatured ethyl alcohol (denatured according to formula No.30, Regulation No. 3 and its appendix U.S. Bureau of Internal Revenue) shall be used for separating cesium.

12. 12.1N Hydrochloric Acid - Concentrated hydrochloric acid (HCl).

13. Silicotungstic Acid Solution - Dissolve 425 grams of silicotungstic acid ($SiO_2 12WO_3 \cdot 26H_2O$) in water and dilute to 1-liter with water.

14. Rubidium Carrier (10 mg/ml) - Refer to Section II on standardization of carriers.

15. (1-2) Hydrochloric Acid - Measure 1 volume of concentrated hydrochloric acid to 2 volumes of water.

D. PROCEDURE

1. Add 2.0 ml cesium carrier and 5 ml concentrated hydrochloric acid to the sample to be analyzed.

2. Add 1 ml of rubidium carrier and 1 ml of silicotungstic acid and allow the solution to stand for 5 minutes with occasional stirring.

D. PROCEDURE (Cont'd)

3. Centrifuge for 3 minutes and discard the supernate.

4. Wash the precipitate twice with 10 ml of (1-2) hydrochloric acid.

5. Dissolve the precipitate in 2 ml of the 6N sodium hydroxide (NaOH) solution and 5 ml of water.
NOTE: Heat gently if it is necessary to put precipitate in solution.

6. Carefully add dropwise 6N hydrochlorc acid until a precipitate forms and add 5 ml excess. Digest on a hot plate and cool.

7. Centrifuge for 2 minutes and transfer the supernate into a clean 50 ml centrifuge tube.
NOTE: Discard the yellow WO_3 precipitate to the solid radioactive waste.

8. Add 3 drops each of iron, zirconium and ruthenium carriers to the supernate.

9. Precipitate ruthenium, zirconium and iron carriers by adding 6N sodium hydroxide (NaOH) drops until a flocculent precipitate forms. Add 5 drops in excess.
NOTE: The precipitate formed will be brown.

D. PROCEDURE (Cont'd)

10. Centrifuge for at least 5 minutes and transfer the supernate to a new clean 50 ml centrifuge tube. The original centrifuge tube and precipitate should be disposed of as radioactive waste.

11. Add 3 drops of iron carrier and repeat steps D-9 and D-10.

12. Add 1 drop of methyl red indicator and add 6N hydrochloric acid (HCl) dropwise until a red color appears. NOTE: Swirl to ensure adequate mixing.

13. Add 1 ml of 10% chloroplatinic acid (H_2PtCl_6) and 10 ml ethanol. Swirl and heat to boiling.

14. Cool the centrifuge tube for 30 minutes in a refrigerator or ice bath.

15. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

16. Rinse the centrifuge tube with ethanol and pour the rinsings through the filter.

17. Wash the precipitate with 5 ml each of ethanol and ether.

D. PROCEDURE (Cont'd)

18. Place the filter containing the precipitates in an oven and dry at 110°C for 10-15 minutes. Cool in a desiccator for 10-15 minutes.

19. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

20. Subtract the tare weight of the filter to obtain the weight of the precipitate.

21. Mount the filter on a suitable holder.

NOTE: Suitable holders are described by Overman and Clark in "Radioisotope Technique", McGraw-Hill, 1960.

22. With a gamma-ray spectrometer, radioassay the precipitate.

E. CALCULATIONS

The cesium activity characteristics are as follows:

E. CALCULATIONS (Cont'd)

Isotope	Half-life	Gamma-Ray Energy, Mev.
Cesium-137	29.2 yrs.	.662 (82%)
Cesium-138	32 min.	.138
		.193
		.229
		.411
		.463
		.545
		. 87
		1.01
		1.43 (73%)
		2.20
		2.61
Cesium-136	13 day	.067
		.087
		. 16
		. 27
		. 34
		. 83
		1.065
		1.25
		1.40

CESIUM METHOD

E. CALCULATIONS (Cont'd)

NOTE: If the demineralizer is not functioning properly, cesium-136 will be detected in the effluent of the Ion Exchanger.

1. Determine the disintegration rate for cesium-137 by determining area under the 0.662 Mev photopeak.

2. Determine the disintegration rate for cesium-138 by determining area under the 1.43 Mev photopeak.

3. The disintegration rate of cesium-137 and 138 is calculated using the equation:

$$\text{dpm-ml} \quad \frac{C}{(V)(E)(F_y)}$$

Where:

C = Counts per minute for cesium-137 and 138 each corrected for background counts and extrapolated back to sampling time.

E = Counting efficiency

NOTE: This factor should include the fractional abundance of the gamma ray and the photopeak detection efficiency.

E. CALCULATIONS (Cont'd)

F_y = Fractional chemical yield for the separation.

V = Volume of sample in ml.

4. Plot a decay curve on semilog paper of the corrected counts per minute versus time for cesium-138.

NOTE: A decay curve should be taken over a period of several hours (sample should be counted for cesium-138 at a minimum of one time an hour over a period of four hours) and extrapolated back to sampling time.

STRONTIUM AND BARIUM METHOD

Method No. RC-5

A. SUMMARY OF METHOD

Barium and strontium are separated from fission product mixtures by precipitation with fuming nitric acid. Barium is separated from strontium as the chromate in buffered acetic acid solution and strontium precipitated as strontium oxalate.

NOTE: The only important alkaline earth fission products are barium and strontium.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Glass Fiber Filter - 1 inch diameter x 0.01 inches thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to ± 0.1 mg during filtration and drying.

3. Filter Holder - The filter holder must hold the 1 inch filters rigidly in place during filtration.

NOTE: Care should be taken to clean the holder thoroughly between filtrations to prevent cross-contamination.

B. APPARATUS (Cont'd)

4. Desiccator - The desiccator must hold four 1 inch diameter filters similar to Fisher No. 8-615.

5. Oven - Oven should be gravity convection type and be able to supply uniform heat at 110° C to a ± 0.5° C. (Fisher No. 13-244-1 or equivalent.)

6. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

7. Gamma-Ray Spectrometer - A sodium iodide scintillation detector assembly connected to the appropriate amplifier and pulse height analyzer.

8. Proportional Counting System - A proportional detector connected to appropriate amplifier and scaler type system.

C. REAGENTS AND MATERIALS

1. Purity of Reagents - Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

C. REAGENTS AND MATERIALS (Cont'd)

2. Purity of Water - All water used in preparing the reagents and in standardization of these reagents shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D 1193).

3. Ethyl Alcohol - Either CP ethyl alcohol or denatured ethyl alcohol (denatured according to formula No. 30, Regulation No. 3 and its appendix, U.S. Bureau of Internal Revenue) shall be used for Standardization of the Carriers.

4. Standardized Strontium Carrier - See Section II on Standardization of Carriers.

5. Standardized Barium Carrier - See Section II on Standardization of Carriers.

6. Lanthanum Carrier - Dissolve 31 grams in 1000 ml of water.

7. Iron Carrier (Unstandardized) - Dissolve 1 gram iron metal powder in 50 ml concentrated hydrochloric acid (HCl) plus 50 ml water.

8. 6M Ammonium Hydroxide (NH_4OH) - Measure 400 ml of concentrated ammonium hydroxide (NH_4OH) (14.8M) and dilute to 1-liter.

STRONTIUM AND BARIUM METHOD

C. REAGENTS AND MATERIALS (Cont'd)

9. 6M Nitric Acid (HNO_3) - Measure 384 ml of concentrated nitric acid (15.7N) (HNO_3) and dilute to 1-liter with water.

10. 6M Acetic Acid - Measure 200 ml concentrated acetic acid ($HC_2H_3O_2$)(17.4N) and dilute to 500 ml with water.

11. 1.5M Sodium Chromate (Na_2CrO_4) - Dissolve 243 grams of sodium chromate (Na_2CrO_4) in water and dilute to 1-liter with water.

12. 6M Ammonium Acetate - Dissolve 230 grams of ammonium acetate ($NH_4C_2H_3O_2$) in water and dilute to 500 ml with water.

13. Concentrated Ammonium Hydroxide - Normality of concentrated reagent is 14.8N.

D. PROCEDURE

1. Add to 50 ml glass centrifuge tube 2 ml standardized strontium carrier, 2 ml standardized barium carrier, 2 ml unstandardized lanthanum.

NOTE: Sample size should be chosen to contain 2000-6000 strontium beta counts per minute at 2π geometry.

2. Add 30 ml of red fuming nitric acid (HNO_3) and stir for 1-2 minutes.

NOTE: Step D-2 should be cooled in an ice bath.

STRONTIUM AND BARIUM METHOD

D. PROCEDURE (Cont'd)

3. Centrifuge for 2 minutes and discard supernate to a plastic waste bottle --- at least 1/2 full of water.

4. Dissolve the precipitate in about 2 ml water and add 15 ml red fuming nitric acid (HNO_3). (Cool in an ice bath during this operation).

NOTE: To dissolve the precipitate, heating may be necessary to effect complete solution.

5. Repeat step D-3.

6. Dissolve precipitate in 5-10 ml water and add approximately 1 ml iron carrier (unstandardized) and 2 ml 6M ammonium hydroxide (NH_4OH).

NOTE: $Fe(OH)_3$ scavenging precipitation is made to remove contaminating activities.

7. Centrifuge and decant supernate to a new glass 50 ml centrifuge tube. Discard the precipitate.

NOTE: Note day and time at this step. Date and time is necessary to make correction in calculation for Yttrium 90 growth.

8. Neutralize supernate to alk-acid paper by adding 6M nitric acid (HNO_3) dropwise.

D. PROCEDURE (Cont'd)

9. Add 1 ml 6M acetic acid and 2 ml ammonium acetate.

10. Heat to incipient boiling, while stirring, add 1 ml of 1.5M sodium chromate (Na_2CrO_4).

NOTE: Barium is separated from strontium as the chromate. Strontium remains in solution.

11. Centrifuge for 2 minutes and decant supernate to a new clean glass centrifuge tube.

12. Save the precipitate from step D-11 and rinse the centrifuge tube with ethyl alcohol and pour the rinsings onto a weighed glass fiber filter placed in the filter holder.

13. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

14. Place the filter containing the precipitate in an oven and dry at 110° C for 20 minutes. Cool in a desiccator for 10-15 minutes.

15. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

16. Subtract the tare weight of the filter to obtain the weight of the precipitate.

D. PROCEDURE (Cont'd)

17. Mount the filter on a suitable holder.

NOTE: Suitable holders are described by Overman and Clark in "Radioisotope Techniques", McGraw-Hill, 1960.

18. With a gamma-ray spectrometer, radioassay the precipitate.

19. To the clear supernate from step D-11, add 2 ml concentrated ammonium hydroxide (NH_4OH).

20. Heat to incipient boiling and while stirring, slowly add 5 ml saturated ammonium oxalate $(NH_4)_2C_2O_4$.

NOTE: Strontium is precipitated as strontium oxalate ($Sr_2C_2O_4$-H_2O) and weighed as such.

21. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder and repeat steps D-13, D-14, D-15, D-16 and D-17.

22. Beta count using the Proportional Flow Counting System.

E. CALCULATIONS

The barium activity is primarily composed of 83 minutes half-life Ba-139 and 12.8 day half-life Ba-140 activities. Both are beta and gamma emitters. For the Ba-139 determination, count every 15 minutes for 1½ hours by following the

E. CALCULATIONS (Cont'd)

0.165 Mev gamma photopeak. For the Ba-140 determination, if Ba-139 is present, begin counting one day after purification from step D-10. Then wait for two weeks and count daily thereafter for 5 to 10 days.

1. Plot the gamma spectrum.
2. Determine the disintegration rate by determining the area under the 0.165 Mev photopeak for Ba-139.
3. Plot a decay curve on semilog paper of the corrected counts per minute versus time.

NOTE: The counting rate of Ba-139 at sampling time is obtained by extrapolating the 83 minute decay curve back to sampling time.

4. To determine the contribution of 12.8 day half-life Ba-140 to the sample, allow the sample to equilibrate with its 40 hour half-life La-140 daughter over a period of two weeks. Then count daily for five days. The count taken one day after separation may be computed because lanthanum hold-back carrier was used in the separation part of the procedure. (See figure RC-5-1 for the curve on Ba-140 decay and growth of La-140 activity.)

E. CALCULATIONS (Cont'd)

5. The disintegration rate of both Ba-139 and Ba-140 is calculated using the equation:

$$\text{dpm - ml} = \frac{C}{(V)\ (E)\ (F_y)}$$

Where:

C = Counts per minute corrected for background counts.

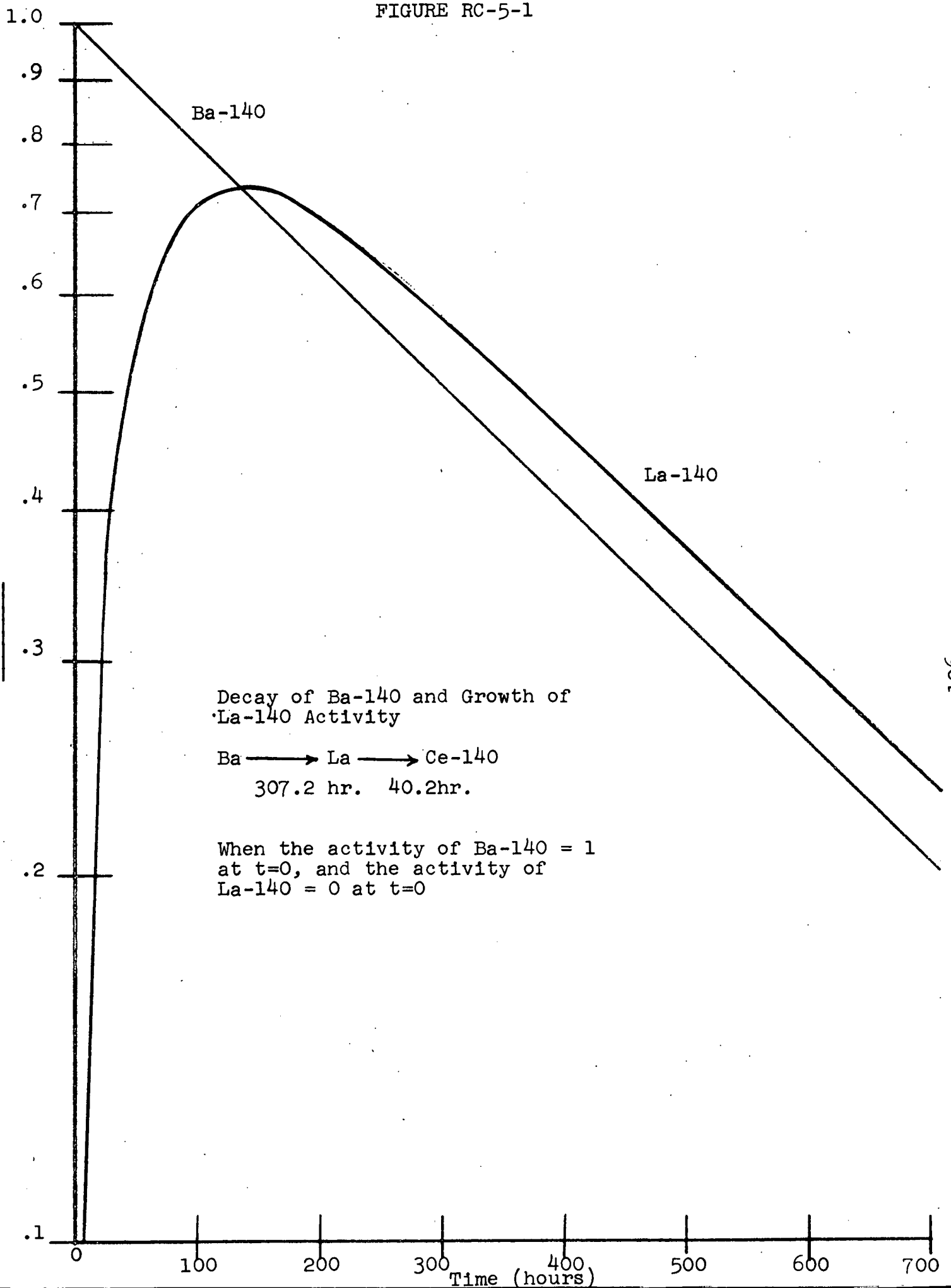
V = Factor for volume of sample.

E = Counting efficiency.

F_y = Yield factor.

6. To determine strontium-90 see method RC-6, Section E.

FIGURE RC-5-1


1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
ACTIVITY
Ba-140
La-140
Decay of Ba-140 and Growth of La-140 Activity
Ba ⟶ La ⟶ Ce-140
307.2 hr. 40.2hr.
When the activity of Ba-140 = 1 at t=0, and the activity of La-140 = 0 at t=0
0
100
200
300
400
500
600
700
Time (hours)

STRONTIUM - 90

Method No. RC-6

A. SUMMARY OF METHOD

The precipitated sample of strontium oxalate monohydrate from procedure RC-5, is disintegrated with fuming nitric acid after addition of yttrium carrier. Strontium and yttrium are coprecipitated as a mixture of oxalate and carbonate salts by the addition of excess sodium carbonate. The precipitate is ignited and then dissolved in nitric acid and then precipitated as yttrium hydroxide. The yttrium hydroxide is dissolved and finally precipitated as yttrium oxalate for weighing and counting.

NOTE: This method should be used if high purification is required.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Glass Fiber Filter - 1 inch diameter x 0.01 inches thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to ± 0.1 mg during filtration and drying.

B. APPARATUS (Cont'd)

3. Filter Holder - The filter holder must hold the 1 inch filters rigidly in place during filtration.

NOTE: Care should be taken to clean the holder thoroughly between filtrations to prevent cross-contamination.

4. Desiccator - The desiccator should hold four 1 inch diameter filters similar to Fisher No. 8-615.

5. Oven - Oven should be gravity convection type and be able to supply uniform heat at 110° C to a ± 0.5° C. (Fisher No. 13-244-1 or equivalent).

6. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

7. Proportional Counting System - A proportional detector connected to appropriate amplifier and scaler type system.

8. Muffle Furnace - To be able to hold four crucibles and also designed for continuous operation at temperatures up to 900° C (1650° F). (Fisher No. 10-552 or equivalent.)

B. APPARATUS (Cont'd)

9. The following additional supplies are needed:

a) 25 ml beaker (6 each)

b) Fine filter paper (Whatman type)

c) 40 ml porcelain crucible (6 each)

d) 100 ml beaker (6 each)

e) 50 ml centrifuge tubes (12 each)

f) 50 ml beaker (6 each)

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D1193).

3. Ammonium hydroxide (14.8N) - Concentrated ammonium hydroxide (NH_4OH).

4. Ethyl Alcohol - Either CP ethyl alcohol or denatured ethyl alcohol (denatured according to formula No. 30, Regulation No. 3 and its appendix, U. S. Bureau of Internal Revenue) shall be used for this method.

C. REAGENTS AND MATERIALS (Cont'd)

5. Ammonium Oxalate Solution ($(NH_4)_2C_2O_4 \cdot H_2O$) - saturated solution.

6. Hydrochloric Acid Solution (1-1) - Mix 1 volume of concentrated (12.N) hydrochloric acid (HCl) with 1 volume of water.

7. Nitric Acid Solution (2-3) - Mix 2 volumes of concentrated (15.7N) nitric acid (HNO_3) with 3 volumes of water.

8. Sodium Carbonate Solution - Dissolve 212 g of sodium carbonate (Na_2CO_3) in water and dilute to 1-liter with water.

9. Strontium Carrier - Refer to Section II on standarization of carrier.

10. Yttrium Carrier - Refer to Section II on standardization of carrier.

11. The following additional chemicals are needed:

a) Ethyl Ether

b) (Red) Fuming Nitric Acid

c) Sodium Carbonate (Na_2CO_3) Solid

STRONTIUM - 90

D. PROCEDURE

1. Place the filter containing the strontium oxalate precipitate in a 25 ml beaker.

2. Add 2.0 ml of standardized yttrium carrier.

3. Add 10 ml of fuming nitric acid (HNO_3) and evaporate to near dryness.

NOTE: After evaporating to near dryness, cool beaker to room temperature.

4. Add 2 ml of fuming nitric acid (HNO_3) and evaporate to near dryness.

5. Add carefully 10 ml of the saturated sodium carbonate (Na_2CO_3) solution and 1 gm of solid sodium carbonate (Na_2CO_3).

6. Boil for 5 minutes on a hotplate and cool to room temperature.

7. Filter the solution through a fine filter paper. After filtering the solution, wash the precipitate with water.

8. Transfer the filter paper containing the precipitate to a porcelain crucible and ignite at 700° C for 1 hour in a muffle furnace.

9. Carefully dissolve the residue in nitric acid (2-3) (HNO3) and transfer to a 100 ml beaker with 20 ml of water.

D. PROCEDURE (Cont'd)

10. Repeat step D-6

11. Add concentrated ammonium hydroxide (NH_4OH) dropwise until yttrium hydroxide precipitates. Add 5 ml in excess and transfer to a 50 ml centrifuge tube.

12. Centrifuge and discard the supernatant.

13. Wash the precipitate twice with 10 ml of water and repeat step D-12 between each wash.

NOTE: Record the date and time afer washing precipitate twice.

14. Dissolve the precipitate in (2-3) nitric acid (HNO_3). Add 2 ml of the strontium carrier solution and repeat steps D11, D12 and D13.

15. Dissolve the precipitate in 2 ml of (1-1) hydrochloric acid (HCl), dilute to 15 ml with water and transfer to a 50 ml beaker.

16. Heat the solution to near boiling and add 20 ml of saturated ammonium oxalate solution. Continue heating for 10 minutes and then cool in an ice bath.

D. PROCEDURE (Cont'd)

17. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

18. Rinse the beaker with ethyl alcohol and pour the rinsings through the filter.

19. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl either.

20. Place the filter containing the precipitate in an oven and dry at 110° C for 20 minutes. Cool in a desiccator for 20 minutes.

21. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

22. Subtract the tare weight of the filter to obtain the weight of the precipitate.

23. Mount the filter on a suitable holder.

NOTE: Suitable holders are described by Overman and Clark in "Radioisotope Techniques" McGraw-Hill 1960.

24. Count the yttrium oxalate precipitate on the proportional flow counting system.

E. CALCULATIONS

1. Calculate the concentration D, of radioactive yttrium-90 in microcuries per cc as follows:

$$D = \frac{C}{2.22 \times 10^6 (E)(V)(R_1)(R_2)}$$

where:

C = beta count rate, in net counts per minute

E = beta counter efficiency in counts per disintegration

V = volume of original sample, in CC

R_1 = fractional chemical yield for the separation of yttrium from Step D-23.

2.22×10^6 = conversion factor from disintegrations per minute to microcuries.

R_2 = fractional chemical yield for the separation of strontium given in Method RC-5.

2. Calculate the decay correction for yttrium-90 as follows:

$$A = A_o e^{-0.693 \frac{t}{T}}$$

where:

A = activity at time sample is counted for yttrium

A_o = activity at time of separation of yttrium from strontium from Step D-13.

t = elapsed time between counting and separation of yttrium from strontium from Step D-13

T = half-life of yttrium, in same unit as t.

E. CALCULATIONS (Cont'd)

3. Calculate the activity of strontium-90 from the growth and separation of yttrium-90 at the beginning of the decay period of strontium-90 as follows:

$$A_o = A\left(\frac{1}{1 - e^{-.693\ \frac{t}{T}}}\right)$$

where:

A_o = Sr-90 activity at the beginning of the decay period of Sr-90.

A = Y^{90} activity at the time yttrium is separated from Sr-90 from Step D-13

t = Sr-90 decay period as determined in Step D-13 in same unit as T.

T = half-life of Sr-90.

Method No. RC-7

A. SUMMARY OF METHOD

Radioiron is isolated in Method RC-10 Step D-10 and eluted from the anion resin column in Step D-2 of this method. This is followed with an acid sulfide scavenge which removes such cation activities as copper. The iron is finally extracted into isoprophyl ether from a hydrochloric acid solution, back extracted into water, precipitated as the hydroxide and ignited to form Fe_2O_3 for radio-assay.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Desiccator - The desiccator must hold four crucibles similar to Fisher No. 8-615.

3. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

4. Gamma-Ray Spectrometer - A sodium iodide scintillation detector assembly connected to the appropriate amplifier and pulse height analyzer.

5. Centrifuge - A clinical centrifuge shall be used. The head should accomodate 50 ml centrifuge tubes.

B. APPARATUS (Cont'd)

6. The following additional supplies are needed:

a) 50 ml centrifuge tube

b) 125 ml separatory funnel

c) Porcelain crucibles

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagent and in diluting the samples shall be demineralized water and conform to the specification for Reagent Water (ASTM Designation D1193).

3. (1-19) Hydrochloric Acid - Mix one volume concentrated hydrochloric acid (HCl) and 19 volumes of water.

4. Copper Carrier (10 mg/ml) - Refer to Section II on standardization of carriers.

C. REAGENTS AND MATERIALS (Cont'd)

5. Iron carrier (10 mg/ml) - Carrier has been added in Method RC-10 Step D-1.

6. 0.5N Hydrochloric Acid - Measure 41.5 of concentrated hydrochloric acid and dilute to 1-liter with water.

7. Hydrogen Sulfide - One laboratory size cylinder of H_2S.

8. Tartaric Acid (saturated solution) - Dissolve 21 gms of tartaric acid in 100 ml of water.

NOTE: Excess solids should be present

9. 6N Ammonium Hydroxide - Measure 305 ml of concentrated ammonium hydroxide (NH_4OH) and dilute to 1-liter with water.

10. 12.1N Hydrochloric Acid - Concentrated hydrochloric acid (HCl).

11. 15.7N Nitric Acid - Concentrated nitric acid (HNO_3).

12. 6N Hydrochloric Acid - Measure 250 ml of concentrated hydrochloric acid and mix with 250 ml of water.

13. Cobalt carrier (10 mg/ml) - Refer to Section II on standardization of carriers.

14. Isoprophyl Ether

15. 14.8N Ammonium Hydroxide - Concentrated ammonium hydroxide.

D. PROCEDURE

1. Place a 50 ml centrifuge cone under the column used in Procedure RC-10.

2. Elute the iron with 10 ml of (1-19) hydrochloric acid HCl from Step D-10 in Procedure RC-10.

3. To the eluate add 10 drops of copper carrier and add 0.5N hydrochloric acid to bring final volume to 20 ml.

4. Saturate with hydrogen sulfide (H_2S) for 1 minute.

NOTE: Place a small bore glass tubing in the solution and bubble the H_2S through the solution.

5. Centrifuge for two minutes and discard the precipitate to the radioactive waste.

6. Add 2 ml saturated tartaric acid ($H_6C_4O_6$) solution and make basic with 6N ammonium hydroxide (NH_4OH) and repeat step D-4.

NOTE: Bring the pH to 8 with NH_4OH (use pH paper).

7. Centrifuge for two minutes and discard the supernate to radioactive waste.

8. Wash the precipitate with 10 ml of water and repeat Step D-7.

D. PROCEDURE (Cont'd)

9. Dissolve the precipitate in 2 ml of concentrated hydrochloric acid (HCl) plus 4 drops of concentrated nitric acid (HNO_3) and boil to near dryness.

10. Bring the volume to 15 ml with 6N hydrochloric acid (HCl) and add 3 drops of cobalt carrier and transfer the solution to a 125 ml separatory funnel.

11. Add 15 ml of isolprophyl ether and shake for 1 minute. CAUTION: Take care to open the stopcock of the separatory funnel during extraction steps to relieve excess pressure.

12. Repeat Step D-11.

13. Combine the greenish-yellow ether layers and wash once with 15 ml of 6N hydrochloric acid (HCl).

14. Back extract the iron with two 10 ml portions of water.

15. Transfer the two 10 ml extract portions into a tared porcelain crucible and add concentrated ammonium hydroxide (NH_4OH) until brown ($Fe(OH)_3$) precipitates.

16. Evaporate to dryness under an infra-red lamp.

17. Ignite in a muffle furnace at 700° C for 15 minutes.

18. Cool in a desiccator and weigh the crucible and precipitate (Fe_2O_3) on an analytical balance to the nearest 0.1 mg.

D. PROCEDURE (Cont'd)

19. Subtract the tare weight of the crucible to obtain the weight of the precipitate.

20. Mount the precipitate on a suitable holder.

21. With a gamma-ray spectrometer, radioassay the precipitate.

E. CALCULATIONS

The iron activity characteristics are as follows:

	Half-Life	Gamma-Ray Energy, Mev.
Iron-59	45 days	1.289 (46%) 1.097 (54%)

1. Determine the disintegration rate for Iron-59 by determining area under the 1.097 Mev. photopeak.

2. The disintegration rate of Iron-59 is calculated using the equation:

$$\text{dpm-ml} = \frac{C}{(V)\ (E)\ (F_y)}$$

E. CALCULATIONS (Cont'd)

where:

C = Counts per minute for Fe-59, corrected for background counter and extrapolated back to sampling time.

E = Counting efficiency

NOTE: This factor should include the fractional abundance of the gamma-ray and the photopeak detection efficiency.

F_y = Fractional chemical yield for separation. (See Method RC-10 Step D-1 for original concentration of iron carrier added).

V = Volume of sample in ml.

CHROMIUM-51

Method No. RC-8

A. SUMMARY OF METHOD

Chromium is oxidized to chromate, scavenged with iron hydroxide ($Fe(OH)_3$) to remove impurities then precipitated as $BaCrO_4$.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Glass Fiber Filter - 1 inch diameter x 0.01 inches thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to $\pm$ 0.01 mg during filtration and drying.

3. Filter Holder - The filter holder must hold the 1 inch filters rigidly in place during filtration.

4. Desiccator - The desiccator must hold four 1 inch diameter filters similar to Fisher No. 8-615.

5. Oven - Oven should be gravity convection type and be able to supply uniform heat at 110° C to a $\pm$ 0.5° C. (Fisher No. 31-244-1 or equivalent).

6. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

B. APPARATUS (Cont'd)

7. Gamma-Ray Spectrometer - A sodium iodide scintillation detector assembly connected to the appropriate amplifier and pulse height analyzer.

8. Centrifuge - A clinical centrifuge shall be used. The head should accomodate 50 ml centrifuge tubes.

9. The following additional supplies are needed:

   a. 50 ml centrifuge tubes

   b. 250 ml beaker

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the specification for Reagent Water (ASTM Designation D 1193).

3. Chromium Carrier (10 mg/ml) - See section II on standardization of carriers.

C. REAGENTS AND MATERIALS (Cont'd)

4. Barium Nitrate (saturated solution) - Dissolve 10 grams barium nitrate $Ba(NO_3)_2$ in 100 ml water.
NOTE: Excess solid should be present.

5. 1M Ammonium Acetate - Dissolve 7.7 grams of ammonium acetate in 100 ml of water.

6. Iron Carrier (10 mg/ml) - See Section II on standardization of carrier.

7. 3N Potassium Hydroxide - Dissolve 88 grams in 500 ml of water.

8. Phenolphthalein - Dissolve 1 gram of phenolphthalein in 50 ml of alcohol and add 50 ml of water.

9. Potassium Bromate ($KBrO_3$)-Solid crystals.

10. 12.1N Hydrochloric Acid - Concentrated hydrochloric acid (HCl).

D. PROCEDURE

1. Add 2 ml chromium and iron carrier to the sample to be analyzed for chromium-51.

2. Add 1 or 2 drops of phenolphthalein solution.

D. PROCEDURE (Cont'd)

3. Add potassium hydroxide (KOH) to the phenolphthalein end-point and heat to coagulate the precipitate for 1 or 2 minutes.

4. Allow to settle briefly for 5 to 10 minutes and decant most of the supernatant liquid to radioactive waste.

5. Transfer the solution containing the precipitate to a 50 ml centrifuge tube and centrifuge for 2 minutes and discard supernate to radioactive waste.

6. Dissolve the precipitate with 4-6 drops of concentrated hydrochloric acid (HCl) (12.1N).

7. Add 15 ml of water and approximately 0.1 gram potassium bromate ($KBrO_3$) crystals.

8. Place the centrifuge tube into a beaker of boiling water. Boil for approximately 10 minutes to oxidize chromium to chromate.

9. Repeat steps D-2 and D-3 and centrifuge for 2 minutes and discard supernate to radioactive waste.

10. Add 4 ml saturated barium nitrate $Ba(NO_3)_2$ and 4 ml of 1M ammonium acetate.

D. PROCEDURE (Cont'd)

11. Centrifuge for 2 minutes and discard supernate to radioactive waste.

NOTE: The precipitate formed is barium chromate $BaCrO_4$.

12. Dissolve the $BaCrO_4$ in approximately 6 drops of concentrated hydrochloric acid HCl plus 10 ml water, dilute to 30 ml and reprecipitate with 5 ml ammonium acetate and 5 ml barium nitrate.

13. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

14. Rinse the centrifuge tube with ethyl alcohol and pour the rinsings through the filter.

15. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

16. Place the filter containing the precipitate in an oven and dry at 110°C for 10-15 minutes. Cool in a desiccator for 10-15 minutes.

17. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

18. Subtract the tare weight of the filter to obtain the weight of the precipitate.

CHROMIUM-51

D. PROCEDURE (Cont'd)

19. Mount the filter on a suitable holder.

NOTE: Suitable holders are described by Overman and Clark in "Radioisotope Technique", McGraw-Hill 1960.

20. With a gamma-ray spectrometer, radioassay the precipitate.

E. CALCULATIONS

The chromium activity is primarily composed of 27.8 day half-life chromium-51.

1. Determine the disintegration rate by determining area under the 0.32 Mev photopeak for Cr-51.

2. Plot a decay curve on semilog paper of the corrected counters per minute versus time.

NOTE: A decay curve should be taken over a period of 2-3 weeks (sample should be counted at a minimum of 2 times a week over a period of 2-3 weeks) and extrapolated back to sampling time.

3. The disintegration rate of chromium-51 is calculated using the equation:

$$\text{dpm-ml} = \frac{C}{(V)\ (E)\ (F_y)}$$

E. CALCULATIONS (Cont'd)

where:

C = counts per minute, corrected for background counts and extrapolated back to sampling time.

E = Counting efficiency.

F_y = Fractional chemical yield for the separation.

V = Volume of sample in ml.

SODIUM-24

Method No. RC-9

A. SUMMARY OF METHOD

Sodium is separated as the chloride after scavenging the solution with strontium, lanthanum and iron carriers.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Glass Fiber Filter - 1 inch diameter x 0.01 inches thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to ± 0.01 mg during filtration and drying.

3. Filter Holder - The filter holder must hold the 1 inch filters rigidly in place during filtration.

4. Desiccator - The desiccator must hold four 1 inch diameter filters similar to Fisher No. 8-615.

5. Oven - Oven should be gravity convection type and be able to supply uniform heat at 110° C to a ± 0.5° C. (Fisher No. 13-244-1 or equivalent).

6. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

B. APPARATUS (Cont'd)

7. Gamma-Ray Spectrometer - A sodium iodide scintillation detector assembly connected to the appropriate amplifier and pulse height analyzer.

8. Centrifuge - A clinical centrifuge shall be used. The head should accommodate 50 ml centrifuge tubes.

9. The following additional supplies are needed:

   a. 250 ml beaker

   b. Hot plate

   c. 50 ml centrifuge tubes

   d. 125 ml Erlenmeyer flask

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the specification for Reagent Water (ASTM Designation D 1193).

C. REAGENTS AND MATERIALS (Cont'd)

3. Sodium Carrier (10 mg/ml) - Refer to Section II on standardization of carriers.

4. Strontium Carrier (10 mg/ml) - Refer to Section II on standardization of carriers.

5. Lanthanum Carrier (10 mg/ml) - Refer to Section II on standardization of carriers.

6. Iron Carrier (10 mg/ml) - Refer to Section II on standardization of carriers.

7. Saturated Ammonium Carbonate Solution - Dissolve 35 grams $(NH_4)_2CO_3 \cdot H_2O$ in 100 ml water.
NOTE: Excess solids should be present.

8. (12.1N) Hydrochloric Acid - Concentrated hydrochloric acid (HCl).

9. Ether

D. PROCEDURE

1. Add sample to be analyzed for sodium to a 250 ml beaker.

2. Add 2 ml sodium carrier to the coolant sample and evaporate on a hot plate to about 25 ml.

D. PROCEDURE (Cont'd)

3. Transfer to a 50 ml centrifuge tube and add 5 drops each of strontium, lanthanum and iron carriers.

4. Add a saturated ammonium carbonate solution dropwise until no more iron hydroxide forms.

NOTE: This iron hydroxide when formed will be a brown gelatinous precipitate.

5. Centrifuge for two minutes and transfer the supernate to a 125 ml Erlenmeyer flask.

6. Add 2 ml concentrated hydrochloric acid (HCl) and evaporate to dryness using a hot plate.

7. Dissolve the residue with 2 ml of water and using 10 ml of concentrated hydrochloric acid (HCl), transfer the dissolved solution to a 50 ml centrifuge tube.

8. Cool the centrifuge in an ice bath and with vigorous stirring add 10 ml ether. Continue to stir for 1-2 minutes.

9. Centrifuge for 2 minutes and discard the supernate to radioactive waste.

10. Dissolve the white precipitate in 2 ml of water and add 10 ml of concentrated hydrochloric acid (HCl).

D. PROCEDURE (Cont'd)

11. Repeat step D-8.

12. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

13. Rinse the centrifuge tube with ethyl alcohol and pour the rinsings through the filter.

14. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

15. Place the filter containing the precipitate in an oven and dry at 110° C for 10-15 minutes. Cool in a desiccator for 10-15 minutes.

16. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

17. Subtract the tare weight of the filter to obtain the weight of the precipitate.

18. Mount the filter on a suitable holder.

NOTE: Suitable holders are described by Overman and Clark in "Radioisotope Techniques", McGraw-Hill, 1960.

19. With a gamma-ray spectrometer, radioassay the precipitate.

SODIUM-24

E. CALCULATIONS

The sodium activity is primarily composed of 15.0 hour half-life sodium-24.

1. Determine the disintegration rate by determining area under the 2.75 Mev photopeak for Na-24.

2. Plot a decay curve on semilog paper of the corrected counts per minute versus time.

NOTE: A decay curve should be taken over a period of several hours (sample should be counted at a minimum of 1-time a day over a period of four days) and extrapolated back to sampling time.

3. The disintegration rate of sodium-24 is calculated using the equation:

$$\text{dpm-ml} = \frac{C}{(V)\ (E)\ (F_y)}$$

where:

C = Counts per minute, corrected for background counts and extrapolated back to sampling time.

E = Counting efficiency.

F_y = Fractional chemical yield for the separation.

V = Volume of sample in ml.

COBALT METHOD

(Cobalt 58 and 60)

Method No. RC-10

A. SUMMARY OF METHOD

Cobalt 58 and 60 are separated from other activities by use of an ion-exchange column. The separated cobalt is purified and precipitated as potassium cobaltinitrite. The separated cobalt is then gamma counted using a gamma-ray spectrometer.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Glass Fiber Filter - 1 inch diameter x 0.01 inches thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to $\pm$0.01 mg during filtration and drying.

3. Filter Holder - The filter holder must hold the 1 inch filters rigidly in place during filtration.

NOTE: Care should be taken to clean the holder thoroughly between filtrations to prevent cross-contamination.

4. Desiccator - The desiccator must hold four 1 inch diameter filters similar to Fisher No. 8-615.

5. Oven - Oven should be gravity convection type and be

B. APPARATUS (Cont'd)

able to supply uniform heat at 110°C to a ±0.5°C. (Fisher No. 13-244-1 or equivalent.)

6. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

7. Gamma-Ray Spectrometer - A sodium iodide scintillation detector assembly connected to the appropriate amplifier and pulse height analyzer.

8. Centrifuge - A clinical centrifuge shall be used. The head should accommodate 50 ml centrifuge tubes.

9. Resin Column - Make out of glass tubing or purchase from Corning Glass Co.

10. The following additional supplies are needed:

a. 50 ml centrifuge tubes

b. 250 ml beakers

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give

C. REAGENTS AND MATERIALS (Con't)

the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the specification for Reagent Water (ASTM Designation D 1193).

3. (1-2) Acetic Acid - Mix 1 volume of 17.4N glacial acetic acid with 2 volumes of water.

4. 14.8N Ammonium Hydroxide - Concentrated ammonium hydroxide (NH_4OH).

5. Anion Exchange Resin - 100 to 200 mesh, 4 percent cross-linked strongly basic resin in chloride form.

6. Cobalt Carrier 10 mg/ml - Refer to Section II on standardization of carriers.

7. Chromium Carrier 10 mg/ml - Refer to Section II on standardization of carriers.

8. Iron Carrier 10 mg/ml - Refer to Section II on standardization of carriers.

9. Manganese Carrier 10 mg/ml - Refer to Section II on standardization of carriers.

C. REAGENTS AND MATERIALS (Cont'd)

10. Nickel Carrier 10 mg/ml - Refer to Section II on standardization of carriers.

11. Zinc Carrier 10 mg/ml - Dissolve 10 gms of zinc in the minimum quantity of 2N hydrochloric acid and dilute to 1-liter with water.

12. 12.1N Hydrochloric Acid - Concentrated hydrochloric acid (HCl).

13. (1-1) Hydrochloric Acid - Mix 1 volume of concentrated hydrochloric acid with 1 volume of water.

14. (30 percent) Hydrogen Peroxide - Concentrated hydrogen peroxide (H_2O_2).

15. Potassium Hydroxide Solution - Dissolve 165 gms of potassium hydroxide KOH in 500 ml of water.

16. Solid Potassium Nitrite KNO_2 - Crystals should be used.

17. (1-10) Potassium Hydroxide - Mix 1 volume of C-15 solution with 10 volumes of water.

18. 36.0N Sulfuric Acid - Concentrated sulfuric acid (H_2SO_4).

COBALT METHOD

(Cobalt 58 and 60)

D. PROCEDURE

1. Add to the sample 2 ml each of the following carriers: cobalt, chromium, iron, manganese, nickel and zinc.

2. Add 5 ml of concentrated sulfuric acid H_2SO_4 and digest on a hot plate. (Digest the solution to approximately 5 ml.)

3. Transfer the solution to a 50 ml centrifuge tube and dilute with water to approximately 10 ml.

4. Add (1-10) potassium hydroxide solution until precipitation is complete. Then add 2 drops of hydrogen peroxide H_2O_2.

5. Centrifuge for 2 minutes and discard the supernate to the radioactive waste.

6. Wash the precipitate with water and repeat step D-5.

NOTE: Repeat this step only once.

7. Dissolve the precipitate in 10 ml of concentrated hydrochloric acid (HCl) and evaporate to near dryness. Allow to cool and dissolve the residue in 10 ml of concentrated hydrochloric acid (HCl).

8. Prepare a column about 1 cm in diameter and 10 cm long of C-5 anion exchange resin suspended in hydrochloric acid (HCl). Wash the resin with 50 ml concentrated hydrochloric

D. PROCEDURE (Cont'd)

acid (HCl).

NOTE: Do not drain below the top of the resin.

9. Transfer the sample solution (D-7) to the column and elute with concentrated hydrochloric acid (HCl) until the blue cobalt band almost reaches the bottom of the resin column.

10. Elute the cobalt of the column by pouring (1-1) hydrochloric acid (HCl) through the column and collect the cobalt in a 50 ml centrifuge tube.

NOTE: The concentrated hydrochloric acid fraction contains manganese, chromium and nickel and may be used for the determination of these activities. Iron remains on the column and may be eluted with (1-19) hydrochloric acid.

11. Evaporate the cobalt solution to dryness in the centrifuge tube. Add 1 ml of (1-1) hydrochloric acid (HCl) and two drops of hydrogen peroxide H_2O_2.

12. Dilute to 10 ml with water and add concentrated ammonium hydroxide NH_4OH until the solution is basic.

NOTE: A pink-brown color should appear.

13. Add 4 drops of iron carrier and centrifuge for 2 minutes

D. PROCEDURE (Cont'd)

and discard the precipitate to the solid radioactive waste.

14. Repeat step D-13.

15. Add two drops of hydrogen peroxide H_2O_2 to the solution and warm.

16. Add (1-10) potassium hydroxide KOH solution dropwise to the solution until a precipitate forms. Place the centrifuge tube in a water bath and boil.

17. Cool and centrifuge for two minutes and discard the supernate to the radioactive waste.

CAUTION NOTE: Carefully retain precipitate.

18. Wash the precipitate with (1-10) potassium hydroxide KOH solution and discard the washings to waste.

19. Dissolve the precipitate in 5 ml of (1-2) acetic acid and dilute with water to 10 ml and add 0.5 gm of potassium nitrite KNO_2.

20. Heat the mixture to near boiling, and cool in an ice bath for about 15 minutes.

21. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

D. PROCEDURE (Cont'd)

22. Rinse the centrifuge tube with ethyl alcohol and pour the rinsings through the filter.

23. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

24. Place the filter containing the precipitate in an oven and dry at 110°C for 10 -15 minutes. Cool in a desiccator for 10-15 minutes.

25. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

26. Subtract the tare weight of the filter to obtain the weight of the precipitate.

27. Mount the filter on a suitable holder.

NOTE: Suitable holders are described by Overman and Clark in "Radioisotope Techniques", McGraw-Hill, 1960.

28. With a gamma-ray spectrometer, radioassay the precipitate.

E. CALCULATIONS

The cobalt activity characteristics are as follows:

COBALT METHOD

(Cobalt 58 and 60)

Isotope	Half-life	Gamma-Ray Energy, Mev
Cobalt-58	71 days	0.808 (100%)
Cobalt-60	5.27 years	1.17 (100%) 1.33 (100%)

1. Determine the disintegration rate for cobalt-58 by determining area under the 0.808 Mev photopeak.

2. Determine the disintegration rate for cobalt-60 by determining area under the 1.33 Mev photopeak.

3. The disintegration rate of cobalt-58 and 60 is calculated using the equation:

$$\text{dpm-ml} = \frac{C}{(V)\ (E)\ (F_y)}$$

where:

C = counts per minute for cobalt-58 and 60 each, corrected for background counts and extrapolated back to sampling time

E = counting efficiency

NOTE: This factor should include the fractional abundance of the gamma ray and the photopeak detection efficiency.

F_y = fractional chemical yield for the separation

V = volume of sample in ml.

NICKEL METHOD

(Nickel 57 and 65)

Method No. RC-11

A. SUMMARY OF METHOD

Radionickel is separated in Method RC-10 Step D-9 using an anion resin column. This is then followed by concentrating the nickel by precipitation with potassium hydroxide. Scavenging is carried out with iron hydroxide ($Fe(OH)_3$) in presence of excess ammonium hydroxide (NH_4OH). The nickel is finally precipitated as nickel dimethylglyoxime.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Glass Fiber Filter - 1 inch diameter x 0.01 inches thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to ± 0.01 mg during filtration and drying.

3. Filter Holder - The filter holder must hold the 1 inch filters rigidly in place during filtration.

NOTE: Care should be taken to clean the holder thoroughly between filtrations to prevent cross-contamination.

4. Desiccator - The desiccator should hold 1 inch diameter filters similar to Fisher No. 8-615.

B. APPARATUS (Cont'd)

5. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

6. Oven - Oven should be gravity convection type and be able to supply uniform heat at 110°C to a ± 0.5° C. (Fisher No. 13-244-1 or equivalent).

7. Gamma-Ray Spectrometer - A sodium iodide scintillation detector assembly connected to the appropriate amplifier and pulse height analyzer.

8. Centrifuge - A clinical centrifuge shall be used. The head should accommodate 50 ml centrifuge tubes.

9. The following additional supplies are needed.

a) 250 ml beaker

b) Hot plate

c) 50 ml centrifuge tubes

C. REAGENTS AND MATERIALS

1. Purity of Reagents - Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specification of the Committee of Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

C. REAGENTS AND MATERIALS (Cont'd)

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D1193).

3. Nickel Carrier (10mg/ml) - Refer to Section II on standardization of carriers.

4. Cobalt Carrier (10 mg/ml) - Refer to Section II on standardization of carriers.

5. Iron Carrier (10 mg/ml) - Refer to Section II on standardization of carriers.

6. IN Potassium Hydroxide - Dissolve 59 gms of potassium hydroxide in water and dilute to 1 liter with water.

7. Phenolphthalein Indicator - Dissolve 1 gm of phenolphthalein in 50 ml of alcohol and add 50 ml of water.

8. 6N Hydrochloric Acid - Mix 1 volume of concentrated hydrochloric acid with 1 volume of water.

9. 14.8N Ammonium Hydroxide - Concentrated ammonium hydroxide (NH_4OH).

C. REAGENTS AND MATERIALS (Cont'd)

10. 10% Sodium Citrate Solution - Dissolve 10 gms of sodium citrate in 90 ml of water.

11. 1% Dimethylglyoxime Reagent - This solution can be purchased from Fisher Chemical Co. Cat. No. SO-D-52.

D. PROCEDURE

1. Transfer the eluate from Method RC-10 Step D-9 to a 250 ml beaker.

2. Add 8 drops of iron carrier and 1-2 drops of phenolphthalein.

3. Add dropwise pottasium hydroxide until a pink color appears.

4. Warm to coagulate the precipitate.

5. Cool and allow precipitate to settle and decant the clear supernate to the radioactive waste. Slurry the precipitate into a 50 ml centrifuge tube.

6. Centrifuge for two minutes and discard the supernate to the radioactive waste.

7. Dissolve the precipitate in 1 ml of 6N hydrochloric acid (HCl) and dilute to 20 ml with water.

8. Heat and add dropwise concentrated ammonium hydroxide until iron is precipitated (brown precipitate appears) and add 1 ml in excess of ammonium hydroxide to dissolve nickel as the ammonia complex.

D. PROCEDURE (Cont'd)

9. Centrifuge for two minutes and transfer supernate to a clean centrifuge tube. Discard the precipitate to the radioactive waste.

10. Acidify the supernate with concentrated hydrochloric acid.

11. Add approximately 8 drops of iron carrier and repeat Steps D-8 and D-9.

12. To the supernate add 10 ml of 10% sodium citrate and 10 drops of cobalt carrier.

13. Add 15 ml dimethylglyoxime reagent.

14. Repeat Step D-6.

15. Wash precipitate with 30 ml of water containing a drop of concentrated ammonium hydroxide NH_4OH and repeat Step D-14.

16. Dissolve the nickel dimethylglyoxime precipitate in 2 ml concentrated hydroxhloric acid and dilute to 15 ml with water.
NOTE: Disregard any dimethylglyoxime which precipitates at this stage.

17. Add 10 ml of 10% sodium citrate, 2 drops of cobalt carrier and 5 ml dimethylglyoxime reagent.

D. PROCEDURE (Cont'd)

18. Precipitate nickel dimethylglyoxime by dropwise adding concentrated ammonium hydroxide.

19. Repeat Steps D-14 and D-15.

20. Repeat Steps D-16, D-17 and D-18.

21. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

22. Rinse the centrifuge tube with water and pour the rinsings through the filter.

23. Wash the precipitate with approximately 10 ml of water.

24. Place the filter containing the precipitate in an oven and dry at 110°C for 15 minutes. Cool in a desiccator for 10-15 minutes.

25. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

26. Subtract the tare weight of the filter to obtain the weight of the precipitate.

27. Mount the filter on a suitable holder.

28. With a gamma-ray spectrometer, radioassay the precipitate.

NICKEL - 57 AND 65

E. CALCULATIONS

The nickel activity characteristics are as follows:

	Half-Life	Gamma Ray Energy, Mev.
Nickel-57	36 hr	1.38 (72%) 1.75 (14%) 1.92 (14%)
Nickel-65	2.56 hr	1.48 (29%) 1.14 (14%)

1. Determine the disintegration rate for Nickel-57 by determining area under the 1.38 Mev photopeak.

2. Determine the disintegration rate for nickel-65 by determining the area under the 1.48 Mev. photopeak.

3. The disintegration rate of Nickel-57 and 65 is calculated using the equation:

$$\text{dpm-ml} = \frac{C}{(V)\ (E)\ (F_y)}$$

where:

C = counts per minute for Nickel-57 and 65 each, corrected for background counts and extrapolated back to sampling time.

E. CALCULATIONS (Cont'd)

E = Counting efficiency

NOTE: This factor should include the fractional abundance of the gamma ray and the photopeak detection efficiency.

F_y = Fractional chemical yield for the separation (29.4 mg nickel dimethylglyoxime per 10 mg nickel).

V = Volume of sample in ml.

4. Plot a decay curve on semilog paper of the corrected counts per minute vs time.

NOTE: A decay curve should be taken over a period of several hours (Nickel-57 should be followed for a week, counting at a minimum of 1 time a day and Nickel-65 should be counted at a minimum of every 2 hours over a period of 24 hours) and extrapolated back to sampling time.

COPPER METHOD

(Copper - 64)

Method No. RC-12

A. SUMMARY OF METHOD

Copper is separated from other activities by precipitating as copper sulfide or by an ion-exchange column technique. The separated copper is then gamma counted using a gamma-ray spectrometer.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Glass Fiber Filter - 1 inch diameter x 0.01 inches thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to ±0.01 mg during filtration and drying.

3. Filter Holder - The filter holder must hold the 1 inch filters rigidly in place during filtration.
NOTE: Care should be taken to clean the holder thoroughly between filtrations to prevent cross-contamination.

4. Desiccator - The desiccator must hold four 1 inch diameter filters similar to Fisher No. 8-615.

5. Oven - Oven should be gravity convection type and be

B. APPARATUS (Cont'd)

able to supply uniform heat at 110° C to a ± 0.5° C. (Fisher No. 13-244-1 or equivalent.)

6. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

7. Gamma-Ray Spectrometer - A sodium iodide scintillation detector assembly connected to the appropriate amplifier and pulse height analyzer.

8. Centrifuge - A clinical centrifuge shall be used. The head should accommodate 50 ml centrifuge tubes.

9. Resin Column - Make out of glass tubing or purchase from Corning Glass Co.

10. The following additional supplies are needed:

a. 50 ml centrifuge tubes

b. 250 ml beakers

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society. Other

C. REAGENTS AND MATERIALS (Cont'd)

reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the specification for Reagent Water (ASTM Designation D 1193).

3. Copper Carrier 10 mg/ml - Refer to Section II on standardization of carriers.

4. Manganese Carrier 10 mg/ml - Refer to Section II on standardization of carriers.

5. Nickel Carrier 10 mg/ml - Refer to Section II on standardization of carriers.

6. Chromium Carrier 10 mg/ml - Refer to Section II on standardization of carriers.

7. Cobalt Carrier 10 mg/ml - Refer to Section II on standardization of carriers.

8. Iron Carrier 10 mg/ml - Refer to Section II on standardization of carriers.

C. REAGENTS AND MATERIALS (Cont'd)

9. Zinc Carrier 10 mg/ml - Dissolve 10 grams of zinc in the minimum quantity of 2N hydrochloric acid (HCl) and dilute to 1-liter with water.

10. Arsenic Carrier (10 mg/ml) - Dissolve 13 grams of arsenic oxide As_2O_3 in 50 ml of 9N hydrochloric acid and dilute to 1-liter with water.

NOTE: Store in a polyethylene bottle.

11. Antimony Carrier (10 mg/ml) - Dissolve 27 grams of anhydrous potassium antimonyl tartrate in 200 ml of (1-2) hydrochloric acid (HCl) and dilute to 1-liter with water.

NOTE: Store in a polyethylene bottle.

12. 12.1N Hydrochloric Acid - Concentrated hydrochloric acid (HCl).

13. 15.7N Nitric Acid - Concentrated nitric acid (HNO_3).

14. Bromine - This solution can be purchased from Fisher Cat. No. B-385.

15. Hydrogen Sulfide (H_2S) - Can be purchased from Fisher as lecture size cylinders, Cat. No. 10-599-L.

COPPER METHOD

C. REAGENTS AND MATERIALS

16. 2M Sodium Hydroxide - Dissolve 40 grams sodium hydroxide in 500 ml of water. (Place in water bath during this operation.)

NOTE: Store in polyethylene bottle.

17. 6M Hydrochloric Acid - Measure 500 ml of concentrated hydrochloric acid and dilute to 1-liter with water.

18. Ion Exchange Resin - Dowex 1 - 4 percent cross-linked - 200 + 500 mesh.

19. 14.8N Ammonium Hydroxide - Concentrated ammonium hydroxide (NH_4OH).

20. 2 Percent - Benzoin Oxime - Dissolve 2 grams of benzoin oxime in 98 ml of ethanol.

D. PROCEDURE

1. Add to the sample 2 ml each of the following carriers - copper, manganese, nickel, chromium, cobalt, iron, zinc, arsenic and antimony.

2. Add 5 ml of concentrated hydrochloric acid and heat to boiling on a hot plate.

COPPER METHOD

D. PROCEDURE (Cont'd)

3. Boil for two minutes after adding 1 drop concentrated nitirc acid (HNO_3) and 5 drops of bromine.

4. Cool and bubble hydrogen sulfide (H_2S) through the solution until a black precipitate is formed.

5. Stir vigorously and allow to stand for 5 minutes.

6. Centrifuge for 2 minutes and discard the supernate to the radioactive waste.

7. Add 5 ml 2M sodium hydroxide (NaOH) and boil for 1 or 2 minutes to digest precipitate.

8. Repeat step D-6.

9. Wash precipitate with water and repeat step D-6.

NOTE: Copper sulfide is the precipitate at this point.

If no cobalt or other activities can be identififed by using a Gamma-ray spectrometer proceed to step D-21.

If activities are detected proceed to step D-10.

10. Dissolve the precipitate in a few drops of concentrated nitric acid (HNO_3) and evaporate to dryness.

11. Add 1 ml concentrated hydrochloric acid (HCl)and evaporate to dryness.

D. PROCEDURE (Cont'd)

12. Dissolve the residue in 6M hydrochloric acid (HCl) and centrifuge for 1 to 2 minutes and discard and precipitate.

13. Bubble hydrogen sulfide (H_2S) through the solution until a black precipitate is formed.

14. Repeat step D-6.

15. Dissolve the precipitate in a few drops of concentrated nitric acid and add 1 ml of cobalt carrier.

16. Evaporate to dryness, and add 2 ml concentrated hydrochloric acid (HCl) and again evaporate to dryness.

17. Dissolve the residue in concentrated hydrochloric acid (HCl) and transfer to a Dowex 1 column.
NOTE: Column approximately 7mm x 15 cms, 4% cross-linked - 200 + 500 mesh previously washed with concentrated hydrochloric acid (HCl).

18. Elute the copper from the column by washing the concentrated hydrochloric acid until yellow copper band is eluted from the column.

19. Evaporate the eluate to dryness and dissolve the residue in 5 ml of 2M hydrochloric acid (HCl); after dissolving the residue add concentrated ammonium hydroxide until the solution is deep blue.

D. PROCEDURE (Cont'd)

20. Heat to about 80° C and add 3 ml of 2% - benzoin oxime solution.

21. Filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

22. Rinse the beaker with water and pour the rinsings through the filter.

23. Wash the precipitate with approximately 5 ml water and two 5 ml portions of hot ethyl alcohol.

24. Place the filter containing the precipitate in an oven and dry at 110° C for 10-15 minutes. Cool in a desiccator for 10-15 minutes.

25. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

26. Subtract the tare weight of the filter to obtain the weight of the precipitate.

27. Mount the filter on a suitable holder.

28. With a gamma-ray spectrometer, radioassay the precipitate.

COPPER METHOD

E. CALCULATIONS

The copper activity is primarily composed of 12.8 hour half-life copper-64.

1. Determine the disintegration rate by determining area under the 0.51 Mev annihalation peak for copper-64.

2. Plot a decay curve on semilog paper of the corrected counts per minute versus time.

NOTE: A decay curve should be taken over a period of several hours (sample should be counted at a minimum of 4 times a day over a period of 2-3 days) and extrapolated back to sampling time.

3. The disintegration rate of copper-64 is calculated using the equation:

$$\text{dpm-ml} = \frac{C}{(V)(E)(F_y)}$$

Where:

C = Counts per minute, corrected for background counts at sampling time.

E = Counting efficiency.

F_y = Yield factor.

E. CALCULATIONS (Cont'd)

NOTE: If precipitated as $Cu(C_{14}H_{11}O_2N)$ the gravimetric yield is 0.2201.

V = Volume of sample in ml.

RADIOACTIVE OFF-GAS ANALYSES

Method No. RC-13

A. SUMMARY OF METHOD

The off-gases are sampled in a counting bottle which is placed directly on the sodium iodide crystal connected to a gamma-ray spectrometer. Gamma-ray count rates are taken at various time intervals.

B. APPARATUS

1. Counting Cell - See Appendix D. The cell should be made of high vacuum glass.

2. Gamma-Ray Spectrometer - A sodium iodide scintillation detector assembly connected to the appropriate amplifier and pulse height analyzer.

C. REAGENTS AND MATERIALS

None

D. PROCEDURE

1. Off-gas is sampled into an evacuated glass Merinelli counting bottle and placed on the sodium iodide crystal.

2. With a gamma-ray spectrometer radioassay the off-gas sample.

E. CALCULATIONS

1. Record gamma count at time intervals.

2. Plot the gamma spectrum.

3. Plot a decay curve on semilog paper of the count rate versus time. Identify isotopes from their half-lifes. You should be alert for 110 minute half-life A-41 from activation of air and noble gas fission products and their daughters; 9 hour half-life Xe-135, 18 minute half-life Rb-88, and 32 minute half-life Cs-138.

It is suggested that time intervals for counting should be every 15 minutes for the first hour then every 30 minutes for the next three hours then once every eight hours for the next twenty-four hours.

GROSS BETA-GAMMA ACTIVITY

Method No. RC-14

A. SUMMARY OF METHOD

A sample of the coolant shall be analyzed by evaporating a sample on a stainless steel planchet and counting on a proportional counter to determine gross Beta-Gamma activity.

B. APPARATUS

1. Evaporator Feeder - To be able to evaporate large volume samples onto a planchet. (See Figure RC-3-1.)

2. Infra-red lamp.

3. 1 each 2 inch diameter stainless steel planchets.

4. Small (clean) forceps.

5. Proportional Counting System - A proportional detector connected to appropriate amplifier and scaler type system.

C. REAGENTS AND MATERIALS

None.

D. PROCEDURE

1. Using an Evaporator Feeder (see section B-1) evaporate 500 ml of the coolant onto a 2 inch diameter stainless steel planchet.

D. PROCEDURE (Cont'd)

2. Count on the proportional flow counter.

E. CALCULATIONS

1. Count for one hour at the Beta voltage setting.

2. Correct for a one hour planchet background and calculate μc/ml as:

$$\mu c/ml = \frac{C}{(2.22 \times 10^6)\ (E)\ (V)}$$

Where:

C = Beta-Gamma count rate, in net counts per minute.

E = Counter efficiency.

V = Volume of original sample in ml.

2.22×10^6 = Conversion factor from disintegrations per minute to micro curies.

NITROGEN-13

Method No. RC-15

A. SUMMARY OF METHOD

Nitrogen-13 is precipitated as ammonium chloroplatinate $(NH_4)_2PtCl_6$, mounted and counted on a proportional flow counter system. The appropriate corrections are made for chemical yield, and radioactive decay since sample was taken.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Glass Fiber Filter - 1 inch diameter x 0.01 inches thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to $\pm$0.01 mg during filtration and drying.

3. Filter Holder - The filter holder must hold the 1 inch filters rigidly in place during filtrations.

4. Desiccator - The desiccator must hold four 1 inch diameter filters similar to Fisher No. 8-615.

5. Oven - Oven should be gravity convection type and be able to supply uniform heat at 110°C to a $\pm$0.5°C. (Fisher No. 13-244-1 or equivalent).

B. APPARATUS (Cont'd)

6. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

7. Centrifuge - A clinical centrifuge shall be used. The head should accommodate 50 ml centrifuge tubes.

8. Proportional Counting System - A proportional detector connected to appropriate amplifier and scaler type system.

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the specification for Reagent Water (ASTM Designation D 1193).

3. Ammonium Carrier (10 mg/ml) - Refer to Section II on standardization of carriers.

4. 18M Sodium Hydroxide - Dissolve 360 grams of sodium hydroxide in 500 ml of water.

C. REAGENTS AND MATERIALS (Cont'd)

5. 5% Chloroplatinic Acid - Dissolve 5 grams chloroplatinic acid crystals ($H_2PtCl_6 \cdot 6H_2O$) in 95 ml of water.

D. PROCEDURE

1. Add sample to be analyzed to a 125 ml Erlenmeyer flask, add 1 ml of ammonium carrier.

2. Add cautiously 5 ml of 18M sodium hydroxide.

3. Set up the distilling apparatus as per figure RC-15-1.

4. Add 2 ml of 5 percent chloroplatinic acid solution to 50 ml centrifuge tube.

5. Dilute to 20 ml with ethyl alcohol and place the centrifuge tube in an ice bath.

6. Place the glass outlet tubing from the Erlenmeyer flask under the surface of the liquid in the centrifuge tube.

7. Gently heat to boiling the 125 ml Erlenmeyer flask containing the sample. Sample should be boiled for three minutes.

8. Disconnect the centrifuge tube and filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

D. PROCEDURE (Cont'd)

9. Rinse the centrifuge tube with ethyl alcohol and pour the rinsings through the filter.

10. Wash the precipitate with approximately 5 ml ethyl alcohol and two 5 ml portions of ether.

11. Place the filter containing the precipitate in an oven and dry at 110°C for 10-15 minutes. Cool in a desiccator for 10-15 minutes.

12. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

13. Subtract the tare weight of the filter to obtain the weight of the precipitate.

14. Mount the filter on a suitable holder.

15. Count on the proportional flow counter or on a Gamma-ray spectrometer.

E. CALCULATIONS

The nitrogen activity is primarily composed of 10 minute half-life nitrogen-13. Nitrogen-13 may be counted both by Beta counting or Gamma counting techniques.

E. CALCULATIONS (Cont'd)

Beta Method

1. Count for 1 minute intervals at the Beta voltage settings.

2. Correct for a 1 minute background and calculate disintegration rate of nitrogen-13 using the following equation:

$$\text{dpm-ml} = \frac{C}{(V)\ (E)\ (F_y)}$$

where:

C = counts per minute for nitrogen-13, corrected for background counter and extrapolated back to sampling time

E = counting efficiency

F_y = fractional chemical yield for the separation

V = volume of sample in ml.

3. Plot a decay curve on semilog paper of the corrected counts per minute vs time.

NOTE: A decay curve should be taken over a period of 30 minutes and extrapolated back to sampling time.

Gamma-Ray Spectrometer Method

1. Determine the disintegration rate by determining the area under the 0.51 Mev annihilation photopeak for N-13.

NOTE: Count for 1 minute intervals.

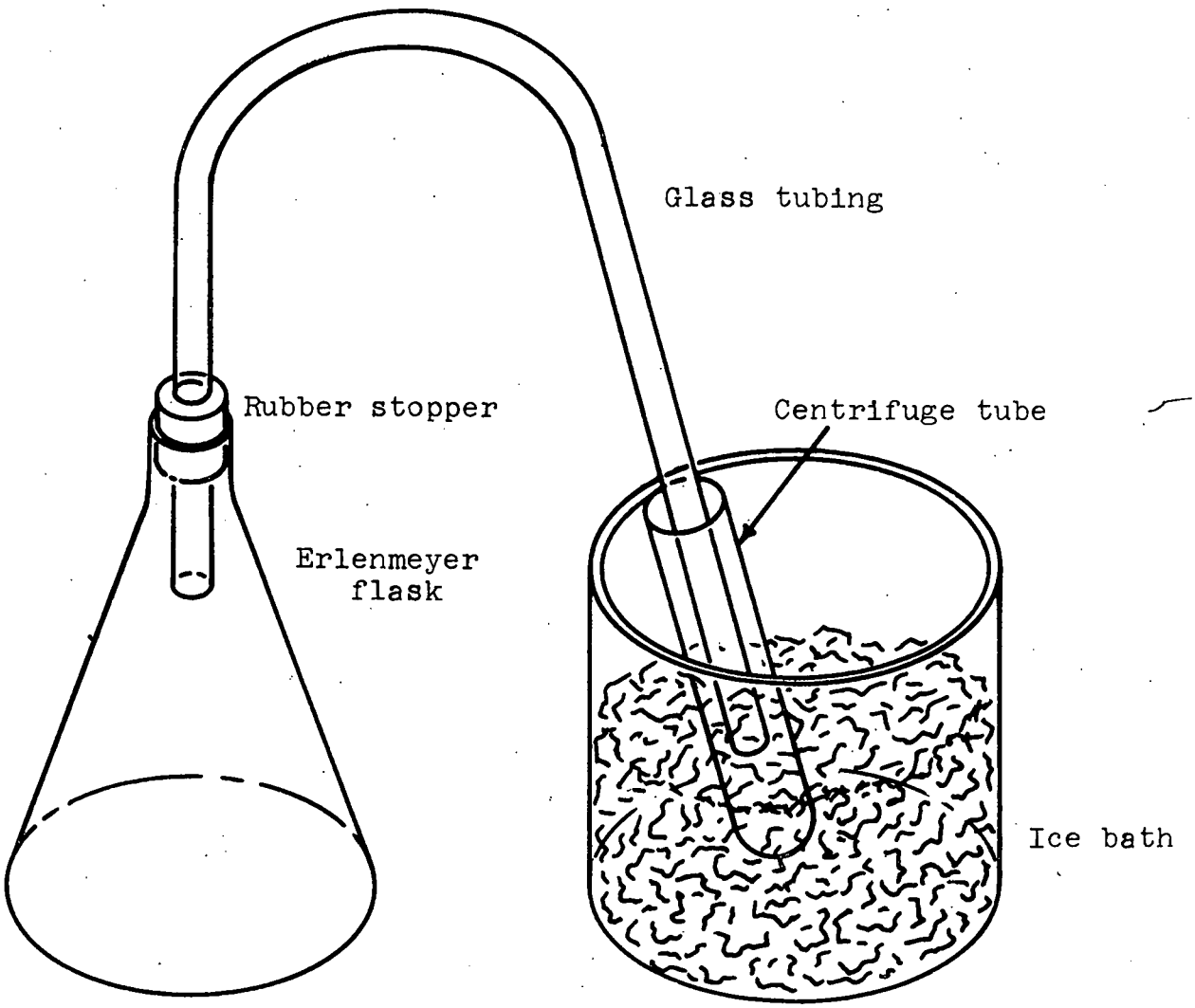
E. CALCULATIONS (Cont'd)

2. To calculate disintegration rate of nitrogen-13 use E-2 equation.

3. Plot a decay curve on semilog paper of the corrected counts per minute vs time.

NOTE: A decay curve should be taken over a period of 30 minutes and extrapolated back to sampling time.

FIGURE RC-15-1



ZIRCONIUM 95

Method No. RC-16

A. SUMMARY OF METHOD

Zirconium is initially separated from the alkali metals and the alkaline earths by a hydroxide precipitation. The soluble ZrF_6 ion is then formed with HF, and the zirconium is reprecipitated from the rare earths as barium flurozirconate. Zirconium is finally precipitated as the mandelate, weighed and counted on a Gamma-ray spectrometer.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Glass Fiber Filter - 1 inch diameter x 0.01 inches thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to $\pm$ 0.01 mg during filtration and drying.

3. Filter Holder - The filter holder must hold the 1 inch filters rigidly in place during filtration.

NOTE: Care should be taken to clean the holder thoroughly between filtrations to prevent cross-contamination.

4. Desiccator - The desiccator should hold four 1 inch diameter filters similar to Fisher No. 8-615.

5. Oven - Oven should be gravity convection type and capable of supplying uniform heat at 110° C to a $\pm$ 0.5° C. (Fisher No. 13-244-1 or equivalent).

6. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

7. Centrifuge - A clinical centrifuge shall be used. The head should accommodate 50 ml centrifuge tubes.

8. Gamma-Ray Spectrometer - A sodium iodide scintillation detector assembly connected to the appropriate amplifier and pulse height analyzer.

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity or give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the specification for Reagent Water (ASTM Designation D 1193).

3. 2N Hydrochloric Acid - Measure 166 ml of hydrochloric acid (HCl) and dilute to 1-liter with water.

4. Zirconium Carrier (10 mg/ml) - Refer to Section II on standardization of carrier solutions.

5. 6N Ammonium Hydroxide - Measure 405 ml of concentrated ammonium hydroxide (NH_4OH) and dilute to 1-liter with water.

6. 15.7 Nitric Acid - Concentrated nitric acid (HNO_3).

7. 48% Hydrofluoric Acid - Concentrated hydrofluoric acid (HF).

8. Saturated Barium Chloride Solution - Dissolve 36 grams of Barium Chloride in 100 ml of water.
NOTE: Excess solid should be present.

9. Saturated Boric Acid - Dissolve 6 grams of boric acid in 100 ml of water.
NOTE: Excess solid should be present.

10. 36N Sulfuric Acid - Concentrated sulfuric acid (H_2SO_4).

11. 2% Aerosol OT Solution - This reagent can be purchased from Fisher Cat. No. SO-A-292.

12. 14.8N Ammonium Hydroxide - Concentrated ammonium hydroxide.

13. (1-1) Ammonium Hydroxide - Measure 1-volume concentrated ammonium hydroxide with 1-volume water.

14. 12.1N Hydrochloric Acid - Concentrated hydrochloric acid (HCl).

15. Methyl Red Indicator - Dissolve 1 gm of methyl red in 600 ml of alcohol and dilute to 1-liter with water.

16. Saturated Ammonium Chloride Solution - Dissolve 32 grams of ammonium chloride in 100 ml of water.

17. 15% Mandelic Acid Solution - Dissolve 15 grams mandelic acid in 85 ml of water.

D. PROCEDURE

1. Add 5 ml of concentrated hydrochloric acid to the sample to be analyzed.

2. Add 2 ml of zirconium carrier and heat to boiling on a hot plate for 1-2 minutes.

3. Cool and add dropwise 6N ammonium hydroxide to precipitate zirconium hydroxide. Add 1-2 ml 6N ammonium hydroxide in excess.

4. Centrifuge for 2 minutes and discard the supernate to the radioactive waste.

5. Dissolve the precipitate by adding 3 ml concentrated nitric acid (HNO_3) and 2 ml of water.

6. Add 3 drops of concentrated hydrofluoric acid (HF) and stir for 1-2 minutes.

7. Centrifuge for 2 minutes and transfer the supernate to a clean 50 ml centrifuge tube. Discard the precipitate to the solid radioactive waste.

8. Add 3 drops of saturated barium chloride solution and repeat step D-4.

CAUTION: Zirconium is precipitated as the insoluble $BaZrF_6$. H_2O barium flurozirconate which is somewhat soluble in acid. Do not add excess Ba and HF which will reduce the solubility.

9. Dissolve the precipitate by adding 4 ml of saturated boric acid (H_3BO_3) solution, stir for 1-2 minutes.

10. Add 2 ml concentrated nitric acid (HNO_3) and dilute to 15 ml with water.

11. To the clear solution, add 6 drops of concentrated sulfuric acid (H_2SO_4) and 2-3 drops of 2% aerosol solution.

12. Centrifuge for 2 minutes and transfer the supernate to a clean centrifuge tube. Discard the precipitate to the radioactive waste.

13. Add 5 ml of concentrated ammonium hydroxide (NH_4OH) to the supernate and repeat step D-4.

14. Wash the precipitate twice with (1-1) ammonium hydroxide (NH_4OH) solution and repeat step D-4.

15. Dissolve the precipitate in 2 ml concentrated hydrochloric acid (HCl) and dilute to 10 ml with water.

16. Add 1-2 drops of methyl red indicator, dropwise add 6N ammonium hydroxide (NH_4OH) until the methyl red endpoint is reached.

NOTE: After the endpoint is reached add 1 drop in excess.

17. Add 2 ml of saturated ammonium chloride (NH_4Cl) solution and dilute to 15 ml with water.

18. Add 10 ml of 15% mandelic acid solution and digest (using a beaker half filled with water placed on a hot plate) for 10 minutes and repeat step D-4.

19. Filter, with suction, the precipitate onto a weighed glass fiber filter placed in the filter holder.

20. Rinse the centrifuge tube with ethyl alcohol and pour the rinsings through the filter.

21. Wash the precipitate with approximately 5 ml ethyl alcohol and two 5 ml portions of ether.

22. Place the filter containing the precipitate in an oven and dry at 110° C for 10-15 minutes. Cool in a desiccator for 10-15 minutes.

23. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

24. Subtract the tare weight of the filter to obtain the weight of the precipitate.

25. Mount the filter on a suitable holder.

26. With a gamma-ray spectrometer radioassay the precipitate.

E. CALCULATIONS

The zirconium activity may consist of 65 day half-life zirconium-95 and 17 hour zirconium-97.

1. Determine the disintegration rate by determining area under the 0.76 Mev photopeak for zirconium-95.

2. Determine the disintegration rate by determining area under the 1.15 Mev photopeak of zirconium-97.

3. For zirconium-97 plot a decay curve on semilog paper of the corrected counts per minute vs time.
NOTE: A decay curve should be taken over a period of several hours (sample should be counted at a minimum of 1-time a day over a period of 4-5 days) and extrapolated back to sampling time).

4. The disintegration rate of zirconium 95 and 97 may be calculated using the equation:

$$\text{dpm-ml} = \frac{C}{(V)\ (E)\ (F_y)}$$

where:

C = Counts per minute, corrected for background counts at sampling time

E = Counting efficiency

F_y = Yield factor

V = Volume of sample in ml.

5. If the sample is not counted within 1-day from the time of radiochemical separation, a correction for the Nb-95 daughter should be made by use of figure RC-16-1 or calculated as follows:

$$A_1 = A_{o_1} e^{-\lambda_1 t}$$

$$A_2 = \frac{\lambda_2 A_{o_1}}{\lambda_2 - \lambda_2} \left(e^{-\lambda_1 t} - e^{-\lambda_2 t} \right)$$

$$F_{Zr\text{-}95} = \frac{A_1}{A_1 + A_2}$$

where:

A_1 = Count rate at Zr-95 at time (t)

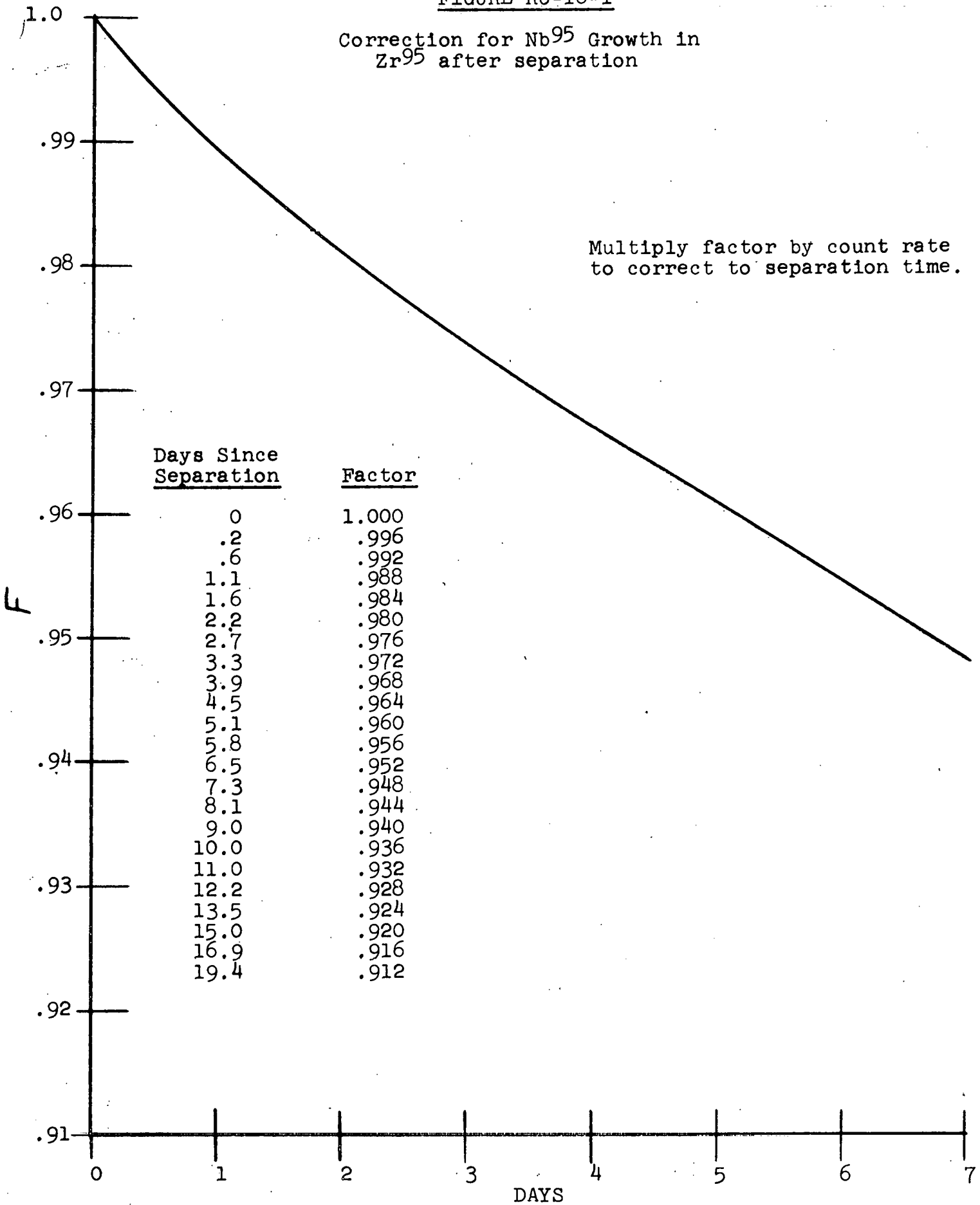
A_{o_1} = Count rate of Zr-95 at time of separation

A_2 = Count rate at Nb-95 at time (t)

FZr95 = Fraction of total gamma originating from Zr-95.

FIGURE RC-16-1

Correction for Nb^{95} Growth in Zr^{95} after separation



Multiply factor by count rate to correct to separation time.

Days Since Separation	Factor
0	1.000
.2	.996
.6	.992
1.1	.988
1.6	.984
2.2	.980
2.7	.976
3.3	.972
3.9	.968
4.5	.964
5.1	.960
5.8	.956
6.5	.952
7.3	.948
8.1	.944
9.0	.940
10.0	.936
11.0	.932
12.2	.928
13.5	.924
15.0	.920
16.9	.916
19.4	.912

FLOURINE - 18

A. SUMMARY OF METHOD — Method No. RC-17

Flourine-18 is precipitated, as (PbFCl) Lead Fluoro Chloride, mounted and counted on a gamma-ray spectrometer counting system or a proportional flow counting system. The appropriate corrections are made for chemical yield, and radioactive decay since sample was taken.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Glass Fiber Filter - 1 inch diameter x 0.01 inches thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to ± 0.01 mg during filtration and drying.

3. Filter Holder - The filter holder must hold the 1 inch filters rigidly in place during filtration.

NOTE: Care should be taken to clean the holder thoroughly between filtrations to prevent cross-contamination.

4. Desiccator - The desiccator should hold four 1 inch diameter filters similar to Fisher No. 8-615.

5. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

6. The following additional supplies are needed:

a. 400 ml beakers

B. APPARATUS (Cont'd)

7. Proportional Counting System - A proportional detector connected to appropriate amplifier and scaler type system.

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the specification for Reagent Water (ASTM Designation D1193).

3. 10% Lead Acetate - Dissolve 10 grams of lead acetate in 90 ml of water.

4. 12.1N Hydrochloric Acid - Concentrated hydrochloric acid (HCl).

5. 15.7N Nitric Acid - Concentrated nitric acid (HNO_3).

6. 17.4N Acetic Acid - Concentrated acetic acid ($HC_2H_3O_2$).

C. REAGENTS AND MATERIALS (Cont'd)

7. Fluorine Carrier (10 mg/ml) - Refer to Section II on standardization of carriers.

8. Methyl Orange Indicator - Dissolve 1 gram of methyl orange in 1 liter water.

D. PROCEDURE

1. To sample add 2 ml fluoride carrier (NaF) and 2-3 drops of methyl orange indicator.

2. Stir while adding concentrated nitric acid dropwise to the solution until a pink color appears.

NOTE: Add three drops of concentrated nitric acid in excess after the end point is reached (pink color appears).

3. Add 16 drops of concentrated hydrochloric acid (HCl) and 10 drops of concentrated acetic acid.

4. Add 25 ml lead acetate solution.

5. Allow to stand briefly until settled and then filter with suction the precipitate onto a weighed glass fiber filter placed in the filter holder.

6. Rinse the centrifuge tube with ethyl alcohol and pour the rinsings through the filter.

D. PROCEDURE (Cont'd)

7. Wash the precipitate with approximately 10 ml ethyl alcohol and 10 ml of diethyl ether.

8. Place filters containing the precipitate in a desiccator for 10 minutes.

9. Weigh the filter and precipitate on an analytical balance to the nearest 0.1 mg.

10. Subtract the tare weight of the filter to obtain the weight of the precipitate.

11. Mount the filter on a suitable holder.

NOTE: Suitable holders are described by Overman and Clark in "Radioisotope Techniques", McGraw-Hill, 1960.

12. Count on the proportional flow counter or on a gamma-ray spectrometer.

E. CALCULATIONS

The fluorine activity is primarily composed of 111 minutes half-life fluorine-18.

Beta Method

1. Count for 5 minute intervals at the Beta voltage setting.

E. CALCULATIONS (Cont'd)

2. Correct for a 5 minute background and calculated disintegration rate of fluorine-18 using the following equation:

$$\text{dpm-ml} = \frac{C}{(V)(E)(F_y)}$$

Where:

C = Counts per minute for F-18, corrected for background counter and extrapolated back to sampling time.

E = Counting efficiency

F_y = Fractional chemical yield for the separation

V = Volume of sample in ml.

3. Plot a decay curve on semilog paper of the corrected counts per minute versus time.

NOTE: A decay curve should be taken over a period of several hours (4-6 hours) and extrapolated back to sampling time.

Gamma-Ray Spectrometer Method

4. Determine the disintegration rate by determining the area under the 0.51 Mev annihilation photo-peak for fluorine-18.

E. CALCULATIONS (Cont'd)

5. To calculate disintegration rate of fluorine-18 use E-2 equation.

6. Repeat step E-3 for determining half-life.

Section VI

DISSOLUTION METHODS

This section is a collection of dissolution procedures for quantitative removal of sorbed activity from ion exchange resins and also the dissolution of insoluble corrosion products which flake off metal surfaces and transported through the cooling system. The dissolution methods have been written for their simplicity of the chemical operations involved.

ION-EXCHANGE RESIN DISSOLUTION

Method No. D-1

A. SUMMARY OF METHOD

Quantitative removal of sorbed activity from ion exchange resins is most effectively accomplished by completely destroying organic resin with concurrent dissolution of all ionic activity in the reactant solution. Hot concentrated sulfuric acid is effective in degrading the resin so that subsequent oxidation with hot concentrated nitric acid (HNO_3) results in complete resin dissolution.

It should be noted that for the recovery of I_2 activity from resin samples refer to Method No. D-2.

B. APPARATUS

1. Hot plate
2. 3 each - 600 ml beakers
3. 1 each - transfer pipettes with rubber bulb attached

C. REAGENTS AND MATERIALS

1. Concentrated nitric acid (15.7N)
2. Concentrated sulfuric acid (36.0N)
3. Standardized carriers for each of the isotopes to be analyzed.

D. PROCEDURE

1. Weigh to the nearest .01 gm approximately 5 grams of air dried resin to be analyzed and place in a 600 ml beaker.

NOTE: Perform the dissolution in triplicate in a fume hood.

2. Add 20 mg of standardized carrier for each of the isotopes undergoing analysis.

3. Add 2 ml of concentrated nitric acid (HNO_3) and cover the beaker with a watch glass.

4. Place beakers on a hot plate and evaporate to dryness.

CAUTION: Use low heat to evaporate to dryness.

5. When the sample is dry, turn the hot plate temperature control to the HIGH position and char the resin.

6. Cool and add 50 ml of concentrated sulfuric acid (H_2SO_4).

7. Place on the hot plate and heat to dense white fumes.

8. Keeping the sample on the hot plate, add concentrated nitric acid (HNO_3) carefully by allowing the HNO_3 to run slowly from a transfer pipette down the side of the beaker.

D. Procedure (Cont'd)

CAUTION: Excess splashing may be avoided by keeping the temperature of the sulfuric acid solution just slightly above the boiling point of the nitric acid (HNO_3).

NOTE: The black mixture will slowly clear, the final solution should be perfectly clear except for insoluble sulfate precipitates such as barium or strontium.

For one gram of resin, 20-30 ml of concentrated nitric acid (HNO_3) should be sufficient.

E. CALCULATIONS

None

IODINE EXTRACTED FROM ION-EXCHANGE RESIN

Method No. D-2

A. SUMMARY OF METHOD

For the specific determination of radioactive metal nuclides, the resin is generally destroyed (Reference D-1 method). The severity of this process used to destroy the resin would result in a complete loss of iodine activities. Therefore, a separate sample of resin should be used for iodine analyses. The iodine activity is removed by oxidation to the molecular state and extracted into carbon tetrachloride. The iodine is finally precipitated as PdI_2 for weighing and counting.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. Glass Fiber Filter - 1 inch diameter x 0.01 inches thick should be used. Any similar filter will be suitable provided it retains fine precipitates adequately and maintains constant weight to $\pm$ 0.1 mg during filtration and drying.

3. Filter Holder - The filter holder must hold the 1 inch filters rigidly in place during filtration.

NOTE: Care should be taken to clean the holder thoroughly between filtrations to prevent cross-contamination.

B. APPARATUS (Cont'd)

4. Desiccator - The desiccator must hold four 1 inch diameter filters similar to Fisher No. 8-615.

5. Oven - Oven should be gravity convection type and be able to supply uniform heat at 110°C to a ± 0.5°C. (Fisher No. 13-244-1 or equivalent).

6. Analytical Balance - It should be capable to weigh to the nearest 0.1 mg.

7. Gamma-Ray Spectrometer - A sodium iodide scintillation detector assembly connected to the appropriate amplifier and pulse height analyzer.

8. The following additional supplies are needed:

a. 1 ea Separatory funnel, 1000 ml Squibb type
b. 2 ea Separatory funnel, 125 ml Squibb type
c. 1 ea 50 ml beaker
d. 1 ea 10 ml graduated cylinder
e. 1 ea 100 ml beaker
f. 1 ea Separatory funnel, 60 ml Squibb type

C. REAGENTS AND MATERIALS

1. Purity of Reagents - Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all

C. REAGENTS AND MATERIALS (Cont'd)

reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used, provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D 1193).

3. Ethyl Alcohol - Either CP ethyl alcohol or denatured ethyl alcohol (denatured according to formula No. 30, Regulations No. 3 and its appendix, U. S. Bureau of Internal Revenue) shall be used for standardization of the carriers.

4. 2M Sodium Carbonate - Dissolve 21 gms sodium carbonate (Na_2CO_3) in 100 ml water.

5. 1M Hydroxyalmine Hydrochloride - Dissolve 7 gms hydroxylamine hydrochloride (NH_2OH-HCl) in 100 ml water.
NOTE: Store in cool place.

6. 1N Nitric Acid (HNO_3) - Measure 64 ml of 15.7N nitric acid (HNO_3) and dilute to 1-liter with water.

7. 0.1M Palladium Chloride - Dissolve 21.4 gms of palladium chloride ($PdCl_2$-$2H_2O$) and dilute to 1-liter with water.

C. REAGENTS AND MATERIALS (Cont'd)

8. 2M Sodium Carbonate (Na_2CO_3) - Dissolve 105 gms sodium carbonate (Na_2CO_3) and dilute with 500 ml water.

9. The additional chemicals are needed:

   a. Carbon tetrachloride (CCl_4)
   b. Conc. Nitric Acid (HNO_3)
   c. Standardized iodine carrier (10 mg/ml)
   d. Sulfurous acid (H_2SO_3)
   e. Sodium nitrite ($NaNO_2$) (solid)
   f. Sodium hyprochlorite (5%) (NaClO)

D. PROCEDURE

1. In a 100 ml beaker containing 2 ml of standardized iodine carrier and 10 ml of 2M sodium carbonate (Na_2CO_3) add 5 gms of air dried resin.

NOTE: Sodium carbonate (Na_2CO_3) keeps the solution alkaline to prevent the formation and subsequent loss of I_2.

2. Add 1 ml of 5% sodium hyprochlorite (NaClO) solution, place in a hot water bath and stir vigorously.

3. Cool the solution and then transfer the solution to a 60 ml separatory funnel.

D. PROCEDURE (Cont'd)

4. To separate iodine - 131 use procedure RC-1 starting on step D-4 thru D-29.

E. CALCULATIONS

Only the 8.05 day I-131 will be present. Analyze I-131 data as stated in procedure RC-1 section E.

DISSOLUTION OF CRUD

Method No. D-3

A. SUMMARY OF METHOD

The crud is insoluble corrosion products that flake off metal surfaces and are transported through the cooling system. The crud is transferred to a porcelain crucible Coors #1 or #2 and ignited over a burner and fused in pyrosulfate dissolved in a hydrochloric acid media and diluted to appropriate volume. After the crud is put into solution, the dissolved crud is then radioassayed for various isotopes.

B. APPARATUS

1. Normal laboratory glassware is required for this work.

2. The following equipment will be needed:
   a. 1 ea - Porcelain crucible, Coors #1 or #2
   b. 1 ea - gas burner (Fisher type burner preferred)
   c. 1 ea - 150 ml beaker
   d. 1 ea - crucible tongs
   e. 1 ea - 50 ml graduated cylinder
   f. 1 ea - hot plate
   g. 1 ea - 50 ml volumetric flask

DISSOLUTION OF CRUD

C. REAGENTS AND MATERIALS

1. Reagent grade chemicals shall be used to prepare reagents. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other reagents may be used provided they are of sufficient purity to give the same accuracy.

2. Purity of Water - All water used in preparing the reagents and in diluting the samples shall be demineralized water and conform to the Specification for Reagent Water (ASTM Designation D 1193).

3. 6M Hydrochloric Acid (HCl) - Measure 100 ml of concentrated (12M) hydrochloric acid (HCl) and dilute with 100 ml water.

4. Solid, potassium pyrosulfate ($K_2S_2O_7$).

D. PROCEDURE

1. Place the filter paper containing the crud in a porcelain crucible.

2. Ignite over the gas burner (low flame until filter paper is completely chared). Turn up gas burner to a medium flame and ignite for 10 minutes.

NOTE: This operation should be performed in a fume hood.

D. PROCEDURE (Cont'd)

3. Cool porcelain crucible and add just enough solid potassium pyrosulfate ($K_2S_2O_7$) to cover the sample.

4. Heat over the gas burner until a cherry red melt is formed.

NOTE: This operation should be performed in a fume hood.

5. Cool the platinum crucible and add 20 ml of 6M hydrochloric acid (HCl).

6. Heat gently on a hot plate until the solid has loosened.

7. After the solid has loosened transfer to a 150 ml beaker and boil until the solid has completely dissolved.

NOTE: Add 6M hydrochloric acid (HCl) if necessary.

8. Cool and dilute the solution to 50 ml with water.

NOTE: If Mn-56 is to be determined use two 25 ml aliquotes.

E. CALCULATIONS

None.

SECTION VII

SCHEDULE FOR RADIO AND WATER CHEMISTRY ANALYSES

A. LACBWR SAMPLING SYSTEM

The LACBWR Sampling System provides the means by which the various Reactor and Generator Plant Auxiliary Systems can be sampled. The sampling program has been designed to supplement plant operating instrumentation.

Routine sampling of the Reactor and Generator Plant Auxiliary Systems enables the plant chemist to:

1. Maintain chemical control within the limits specified in the operating manual and as dictated by good water chemistry control practice to achieve optimum water quality for the protection of plant equipment.

2. Establish base line water chemistry and radiochemistry data for use in the detection and interpretation of abnormal conditions.

3. Calibrate and check station operating instruments.

4. Determine that activation of the system corrosion products from structural materials does not exceed expected values.

SECTION VII

SCHEDULE FOR RADIO AND WATER CHEMISTRY ANALYSES

A. LACBWR Sampling System (Cont'd)

5. Provide efficiency and operational information on the purification demineralizers systems.

In addition to the normal control procedures such as pH, conductivity, and chloride used to determine whether chemical control is operating as designed, the system provides a means for conducting the following chemical tests for gathering a history of plant operation on which to base the detection and interpretation of abnormal conditions:

1. Total Iron and Copper - Determining the level of copper in the reactor coolant, feedwater and full flow condensate systems enables the plant chemist to establish a material balance and to detect abnormal corrosion behavior of components in these systems. Total iron determines relative rate of total system corrosion and total copper determines condenser tubing corrosion.

2. Dissolved Oxygen - Determining the dissolved oxygen concentration in the reactor coolant, feedwater, and full flow condensate systems enables the plant chemist to better understand plant corrosion with special interest focused on reactor components

SECTION VII

SCHEDULE FOR RADIO AND WATER CHEMISTRY ANALYSES

A. LACBWR Sampling System (Cont'd)

subject to chloride stress corrosion cracking and to detect air inleakage.

3. Total Solids - Determining the total solids concentration of the reactor coolant, feedwater and full flow condensate systems enables the chemist to better understand overall plant corrosion behavior and to detect condenser inleakage.

4. Silica - Determining the silica concentration of the feedwater, main steam and the virgin and condensate storage tanks enables the chemist to establish a material balance, to detect condenser inleakage, to insure proper makeup water quality, and the minimization of SiO_2 carryover and turbine blade build-up.

5. Radionuclide Separation - Determining the following list of radionuclides present in the reactor coolant will establish the concentration and types of corrosion-erosion products present in the coolant and also determine if fuel failure occured.

The following are typical radionuclides present in water reactor coolant:

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SCHEDULE FOR RADIO AND WATER CHEMISTRY ANALYSES

A. LACBWR Sampling System (Cont'd)

Coolant Activation Products		Fission Products		Activated Corrosion Products	
Radionuclide	Half-life	Radionuclide	Half-life	Radionuclide	Half-life
N-16	7.35 sec.	I-134	58.0 min.	Mn-56	2.58 hrs.
N-13	10.0 min.	I-135	6.7 hrs.	Ni-65	2.56 hrs.
Ar-41	1.83 hrs.	I-133	21.0 hrs.	Cu-64	12.9 hrs.
F.18	111.0 min.	I-131	8.05 days	W-187	24.0 hrs.
Na-24	15.0 hrs.	Cs-139	9.5 min.	Cr-51	27.8 days
		Cs-138	32.2 min.	Fe-59	45.0 days
		Cs-137	30 yrs.	Zr-95	65.0 days
		Ba-139	83 min.	Co-58	71.0 days
		Ba-140	12.8 days	Co-60	5.27 yrs.
		Sr-91	9.7 hrs.	Mn-54	314.0 days
		Sr-92	2.7 hrs.		
		Sr-89	50.4 days		
		Sr-90	27.7 yrs.		
		Zr-95	65 days		
		Mo-99	66 hrs.		
		Xe-133	5.27 days		
		Xe-135	9.2 hrs.		
		Xe-135m	15 min.		
		Kr-85	10.4 yrs.		

Reactor Purification

The reactor purification system can be sampled at two points: influent and effluent streams.

The influent sample connection, located upstream of cation and mixed bed ion exchanger and downstream of valve 51-24-007, consists of a 1/2" stainless steel pipe and two normally closed 1/2" stainless steel globe valves (51-23-001 and 51-23-002).

The effluent sample connection, which is located upstream of

SECTION VII

SCHEDULE FOR RADIO AND WATER CHEMISTRY ANALYSES

A. LACBWR Sampling system (Cont'd)

51-24-014 and downstream of cation and mixed bed ion exchanger consists of a 1/2" stainless steel pipe and two normally closed 1/2" stainless steel globe valves (51-23-003 and 51-23-004).

Both sample connections terminate over a small stainless steel combination sink-work table located at elevation 621'-0".

Overhead Water Storage Tank

The overhead water storage tank sample point, which is located upstream of the locked closed 3" drain valve 69-24-002 above the main floor, consists of a 1/2" carbon steel pipe and a 1/2" globe valve 69-23-001. The sample connection terminates at the sampling table located at elevation 667'-0".

Boron Injection

The Boron Injection System can be sampled at two points: storage tank and pump suction line.

The storage tank sample connection is located downstream of the tank, and upstream of the locked-open 3" gate valve 60-24-002.

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SCHEDULE FOR RADIO AND WATER CHEMISTRY ANALYSES

Boron Injection (Cont'd)

Both sample points located at elevation 667'-0", and each consists of a 1/2" stainless steel pipe and a 1/2" globe valve (60-23-001 tank sample 60-23-002 pump suction line sample).

The injection line sample point just upstream of auto control valve 60-25-001 is useful in detecting any crystallization of the sodium pentaborate in the suction line.

Shield Cooling

The Shield Cooling System sample point, located on the shield cooling pump discharge header upstream of the shield cooling filter, consists of a 1/2" carbon steel pipe and 1/2" globe valve 59-23-002.

The sample connection terminates over the small combination sink-work table provided for the Reactor Purification System at elevation 621'-0".

Fuel Storage Well

The Fuel Storage Well System can be sampled at two points at elevation 642'-9". One sample point is located upstream of the filter, and downstream of the skimmer and overhead storage tank connections. (58-23-003) Another sample point is located on the return line, immediately upstream of the

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SCHEDULE FOR RADIO AND WATER CHEMISTRY ANALYSES

Fuel Storage Well (Cont'd)

fuel storage well. (58-23-002)

Each sample connection consists of a 1/2" stainless steel pipe and a normally closed 1/2" globe valve (58-23-002 and 58-23-003).

Component Cooling Water

The Component Cooling Water System sample point, located on the component cooling water pump discharge header consists of a 1/2" carbon steel pipe and 1/2" globe valve 57-23-003 at elevation 640'-0" in the Generator Plant.

Liquid Waste

The Liquid Waste Disposal System can be sampled at 8 points:

1. Each of the two 6,000 gallon retention tanks (1A and 1B) has a bottom sample connection consisting of 1" carbon steel pipe and a 1" bronze globe valve (54-23-006 "1A" and 54-23-007 "1B"). Both sample connections terminate over the combination sink-work table located at elevation 621'-0".

2. The 3000 gallon waste water storage tank has a bottom sample connection consisting of a 1" carbon steel pipe and 1" bronze globe valve 54-23-008.

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SCHEDULE FOR RADIO AND WATER CHEMISTRY ANALYSES

Liquid Waste (Cont'd)

3. The 4500 gallon waste water storage tank has a bottom sample connection consisting of a 1" carbon steel pipe and 1" bronze globe valve 54-23-009 which terminates outside the shielding wall which surrounds the tank.

4. The evaporator feed tank has a bottom sample connection consisting of 1/2" stainless steel pipe which is extended outside the shielding well and 1/2" stainless steel globe valve 54-23-013.

5. The 1 gpm waste evaporator has a bottom sample connection consisting of 1" stainless steel pipe and a 1" stainless steel extended stem ball valve 54-23-011.

6. The spent resin tank has a bottom sample connection consisting of 1/2" stainless steel pipe extended outside the shield wall and 1/2" stainless steel ball valve 54-23-014.

7. The water collection tank has a bottom sample connection consisting of 1" carbon steel pipe and 1" bronze globe valve 54-23-005.

8. The 500 gallon concentrated waste storage tank has a bottom sample connection consisting of 1"

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SCHEDULE FOR RADIO AND WATER CHEMISTRY ANALYSES

Liquid Waste (Cont'd)

stainless steel pipe and a 1" extended stem and handwheel diaphragm valve 54-23-012.

The evaporator and evaporator feed tank sample points terminate at a central sampling station located over a sample trough just outside the shield wall in the waste disposal building. The spent resin tank sample point will extend down into the basement. The water collection tank sample point will be located at the tank.

Gaseous Waste System

The Gaseous Waste System can be sampled at four points: two for gaseous content, and two for condensed moisture.

The two 1600 cu. ft. gas storage tanks, located in the underground gas storage vault, have a common bottom sample connection consisting of a 1/4" carbon steel pipe and 1/4" carbon steel globe valve, 55-23-008. This bottom sample connection together with tank drain valves 55-23-006 and 007, are used to sample the condensed moisture in the tanks.

In addition, each gas storage tank has a top sample connection consisting of a 1/4" carbon steel piping and 1/4"

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Gaseous Waste System (Cont'd)

carbon steel needle valves, 55-23-011 (Tank. No. "1B") and 55-23-010 (Tank No. "1A"). These top sample connections are used to sample the gaseous contents of the tanks.

The two gaseous sample lines terminate over a sample trough on a table in the waste disposal building.

Shutdown Condenser

The Shutdown Condenser can be sampled at two points: shell side coolant and condensate return.

The shell side sample connection, located upstream of drain valve 62-24-018 consists of a sample cooler, 1/2" carbon steel pipe and 1/2" bronze globe valves 62-23-003 and 62-23-004.

Feedwater

The Feedwater System sample point, located at elevation 621'-0", consists of a sample cooler, 1/2" stainless steel pipe and two normally closed 1/2" stainless steel globe valves 65-23-001 and 65-23-002, which are located downstream of valve 65-24-001.

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SCHEDULE FOR RADIO AND WATER CHEMISTRY ANALYSES

Main Steam

The Main Steam Sampling arrangement, located at elevation 667'-0", consists of an ASME sample nozzle, a throttling calorimeter and a sample cooler.

The throttling calorimeter is used to measure steam quality.

The condensed steam leaving the sample cooler can be sampled via a 1" stainless steel pipe and two 1" stainless steel globe valves (64-23-001 and 64-23-002).

Full-Flow Condensate Demineralization

The Full-Flow Condensate Demineralization System can be sampled at four points: One common sample point in the influent stream and a separate sample point in the effluent stream for each of the three mixed-bed demineralizers.

The common influent sample connection is located on the condensate pump discharge header downstream of conductivity element and upstream of the three demineralizers. It consists of a 1/2" carbon steel pipe and two 1/2" carbon steel globe valves.

Each effluent leg of the three demineralizers is fitted with a 1/2" carbon steel pipe and two 1/2" carbon steel globe valves located downstream of the extended stem

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SCHEDULE FOR RADIO AND WATER CHEMISTRY ANALYSES

Full-Flow Condensate Demineralization (Cont'd)

handwheel effluent valves.

Demineralized Makeup and Well Water

The Demineralized Makeup and Well Water System can be sampled at five points.

The deep well water supply sample connection, located downstream of the deep well pumps and upstream of the cation exchanger, consists of a 1/2" line and a 1/2" globe valve.

The cation exchanger sample connection is located on the demineralizer effluent line and consists of a 1/2" line and a 1/2" globe valve.

The anion exchanger sample connection is located on the demineralizer effluent line and consists of a 1/2" line and a 1/2" globe valve.

B. RADIO AND WATER CHEMISTRY TESTS

The water chemistry limits shown on Table VII-I are those recommended for normal plant operation. Normal operation is defined when the plant turbine is at 20 percent load or above. Radio and Water Chemistry tests shown without

SECTION VII

SCHEDULE FOR RADIO AND WATER CHEMISTRY ANALYSES

B. RADIO AND WATER CHEMISTRY TESTS (Cont'd)

limits are those tests which are conducted to gain base line operational data.

RADIO AND WATER CHEMISTRY TESTS SCHEDULE

TABLE VII-1

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number	Sample Aliquote (ml)
1 REACTOR PURIFICATION						
Influent Sample	51-23-002 51-23-001	pH	3 times/wk.	7.0 ± 0.5	WC-1	250
		Conductivity (μmhos-Cm)	3 times/wk.	1.0 max.	WC-2	250
		Chloride (ppm)	3 times/wk.	0.1 max.	WC-3	25
		Copper (ppm)	once/ wk.		WC-12	50
		Iron (ppm)	once/wk		WC-4	50
		Dissolved Oxygen (ppm)	once/wk.	2.0 ± 2	WC-8A	See Method
		Silica (ppm)	once/wk.		WC-16	50
		Radiochemical Iodine (dpm-ml)	once/wk.		RC-1	
		Gross Alpha Activity (dpm-ml)	once/wk.		RC-3	
		Gross β-γ Activity (dpm-ml)	once/wk.		RC-14	
		Gamma-ray Spectrum of Water	once/wk.			
		Dissolved Solids (ppm)	once/mo.		WC-6	See Method
		Suspended Solids (ppm)	once/mo.		WC-5	1000
		Total Solids (ppm)	once/mo.		WC-7	100
		Radiochemical Manganese (dpm-ml)	6 times/yr.		RC-2	
		" Cesium (dpm-ml)	6 times/yr.		RC-4	
		" Strontium "	once/mo.		RC-5	
		" Iron "	once/mo.		RC-7	
		" Chromium "	once/mo.		RC-8	
		" Sodium "	once/mo.		RC-9	
		" Cobalt "	6 times/yr.		RC-10	
		" Nickel "	6 times/yr.		RC-11	
		" Copper "	6 times/yr.		RC-12	
		" Zirconium "	6 times/yr.		RC-16	
		" Nitrogen "	once/mo.		RC-15	
		" Fluorine "	once/mo.		RC-17	
Effluent Sample	51-23-003 51-23-004	pH	3 times/wk.	7.0 ± 0.5	WC-1	250
		Conductivity (μ mhos-Cm)	3 times/wk.	1.0 max.	WC-2	250
		Chloride (ppm)	3 times/wk.	0.1 max.	WC-3	25

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number	Sample Aliquote (ml)
Effluent Sample (Cont'd)		Copper (ppm)	once/wk.		WC-12	50
		Iron (ppm)	once/wk.		WC-4	50
		Dissolved Oxygen (ppm)	once/wk.	2.0 ± 2	WC-8A	See Method
		Silica (ppm)	once/wk.		WC-16	50
		Radiochemical Iodine (dpm-ml)	once/wk.		RC-1	
		Gross Alpha Activity (dpm-ml)	once/wk.		RC-3	
		Gross β-γ Activity (dpm-ml)	once/wk.		RC-14	
		Gamma-ray Spectrum of water	once/wk.			
		Suspended Solids (ppm)	once/mo.		WC-5	1000
		Total Solids (ppm)	once/mo.		WC-7	100
		Radiochemical Manganese (dpm-ml)	6 times/yr.		RC-2	
		" Cesium "	6 times/yr.		RC-4	
		" Strontium "	once/mo.		RC-5	
		" Iron "	once/mo.		RC-7	
		" Chromium "	once/mo.		RC-8	
		" Sodium "	once/mo.		RC-9	
		" Cobalt "	6 times/yr.		RC-10	
		" Nickel "	6 times/yr.		RC-11	
		" Copper "	6 times/yr.		RC-12	
		" Zirconium "	6 times/yr.		RC-16	
		" Nitrogen "	once/mo.		RC-15	
		" Fluorine "	once/mo.		RC-17	
II. OVERHEAD WATER STORAGE TANK	69-23-001	p^H	once/mo.	7.0 ± 1.0	WC-1	250
		Conductivity (μ mhos-Cm)	once/mo.	1.5 ± 1.5	WC-2	250
		Chloride (ppm)	once/mo.	0.1 max.	WC-3	250
		Gross Activity (dpm-ml)	once/mo.		RC-14	
III. BORON INJECTION TANK SAMPLE	60-23-001	Boron (w/o)	once/mo.	17.8	WC-11B	1000
IV. SHIELD COOLING	59-23-002	p^H	once/mo.	10 ± 0.5	WC-1	250
		Conductivity (μ mhos-Cm)	once/mo.	41 ± 34	WC-2	250
		Total Solids (ppm)	once/mo.	20 ± 20	WC-7	100
		Dissolved Solids (ppm)	once/mo.		WC-6	See Method
		Suspended Solids (ppm)	once/mo		WC-5	1000
		Gross β-γ Activity (dpm-CC)	once/mo.	1×10^{-7} max.	RC-14	
		Gamma-ray Spectrum of Water	once/mo.			
		Chloride (ppm)	once/mo.	0.1 max.	WC-3	25

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number	Sample Aliquote (ml)
V FUEL STORAGE WELL						
Upstream of filter	58-23-003	pH	once/mo.	7.0 ± 1.0	WC-1	250
		Conductivity (μ mhos-Cm)	once/mo.	3 ± 2	WC-2	250
		Chloride (ppm)	once/mo	0.1 max.	WC-3	25
		Dissolved Solids (ppm)	once/mo.	3 ± 3	WC-5	1000
		Suspended Solids (ppm)	once/mo.		WC-6	See Method
		Total Solids (ppm)	once/mo.		WC-7	100
		Gross β-γ Activity (dpm-ml)	once/wk.		RC-14	
		Gamma-ray Spectrum of Water	once/wk.			
Return line	58-23-002	pH	once/mo.		WC-1	250
		Conductivity (μm hos-cm)	once/mo.		WC-2	250
		Chloride (ppm)	once/mo.		WC-3	25
		Dissolved Solids (ppm)	once/mo.		WC-5	1000
		Suspended Solids (ppm)	once/mo.		WC-6	See Method
		Total Solids (ppm)	once/mo.		WC-7	100
		Gross β-γ Activity (dpm-ml)	once/wk.		RC-14	
		Gamma-ray Spectrum of Water	once/wk.			
VI. Component Cooling Water	57-23-003	pH		9.0-10.5	WC-1	250
		Chromate (ppm)	once/mo.	300-400	WC-10	50
		Phosphate (ppm)	once/mo.	25-30	WC-14	50
		Dissolved Solids (ppm)	once/mo.		WC-5	1000
		Suspended Solids (ppm)	once/mo.		WC-6	See Method
		Total Solids (ppm)	once/mo.	1000	WC-7	100
		Gross β-γ Activity (dpm-ml)	once/mo.		RC-14	
VII. LIQUID WASTE						
6,000 gallon	54-23-006	pH	as required		WC-1	250
Retention tank 1A and	54-23-007	Conductivity (μ mhos-Cm)	as required		WC-2	250
Retention tank 1B		Suspended Solids (ppm)	as required		WC-6	See Method
		Total Solids (ppm)	as required		WC-7	100
		Gross β-γ Activity (dpm-ml)	as required		RC-14	
		Gross Alpha Activity (dpm-ml)	as required		RC-3	
		Gamma-ray Spectrum of Water	as required			
3,000 gallon						
Waste Water Storage Tank	54-23-008	pH	as required		WC-1	250
		Conductivity (μmhos-Cm)	as required		WC-2	250
		Suspended Solids (ppm)	as required		WC-6	See Method
		Total Solids (ppm)	as required		WC-7	100
		Gross β-γ Activity (dpm-ml)	as required		WC-14	

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number	Sample Aliquote (ml)
3000 gallon (Cont'd)		Gross Alpha Activity (dpm-ml)	as required		RC-3	
		Gamma-ray Spectrum of Water	as required			
4500 gallon Waste Water storage tank	54-23-009	pH	as required		WC-1	250
		Conductivity (μ mhos-Cm)	as required		WC-2	250
		Suspended Solids (ppm)	as required		WC-6	See Method
		Total Solids (ppm)	as required		WC-7	100
		Gross β-γ activity (dpm-ml)	as required		RC-14	
		Gross Alpha Activity (dpm-ml)	as required		RC-3	
		Gamma-ray Spectrum of Water	as required			
Evaporator Feed Tank	54-23-08	pH	as required	7.0 ± 1.0		
		Conductivity (μmhcs-Cm)	as required		WC-1	
		Gross Activity (uc/cc)	as required	1×10^{-7} max.	RC-14	
		Total Solids (ppm)	as required			
Waste Evaporator (Bottom Sample Connection)	54-23-011	pH	as required	7.0 ± 1.0	WC-1	250
		Total Solids (ppm)	as required		WC-2	250
		Gross β-γ Activity (uc/cc)	as required		RC-14	
Spent Basin Tank	54-23-014	Gross β-γ Activity (uc/cc)	as required		RC-14	
		Radiochemical Iodine (dpm/gm)	as required		D-2 + RC-1	
		Radiochemical Manganese (dpm-gm)	as required		D-1 + RC-2	
		Radiochemical Cesium (dpm-gm)	as required		D-1 + RC-4	
		Radiochemical Strontium (dpm-gm)	as required		D-1 + RC-5	
		Radiochemical Iron (dpm-gm)	as required		D-1 + RC-7	
		Radiochemical Chromium (dpm-gm)	as required		D-1 + RC-8	
		Radiochemical Sodium (dpm-gm)	as required		D-1 + RC-9	
		Radiochemical Cobalt (dpm-gm)	as required		D-1 + RC-10	
		Radiochemical Nickel (dpm-gm)	as required		D-1 + RC-11	
		Radiochemical Copper (dpm-gm)	as required		D-1 + RC-12	
		Radiochemical Zeronium (dpm-gm)	as required		D-1 + RC-16	
		Gamma-Ray Spectrum of Resin	as required			
Water Collection Tank	54-23-005	pH	as required		WC-1	250
		Conductivity (μmhos-Cm)	as required		WC-2	250
		Gross Activity (dpm-ml)	as required		RC-14	
		Gamma-ray Spectrum of Water	as required			
500 gallon Concentrated Waste Storage Tank	54-23-012	pH	as required		WC-1	use pH paper
		Gross β-γ Activity (uc/cc)	as required		RC-14	

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number	Sample Aliquote (ml)
500 gallon (Cont'd)		Gamma-ray Spectrum of Water	as required			
VIII. GASEOUS WASTE						
Sample Condensed Moisture	55-23-008	Gross β-γ Activity (μc/cc)	as required		RC-14	
	55-23-006	Gamma-ray Spectrum of Water	as required			
		Radiochemical Iodine (dpm-ml)	as required		RC-1	
Gaseous Content of Retention Tank 1A-1B	55-23-011	Gaseous Acticity (dpm)	as required		RC-13	
	55-23-010	Gamma-ray Spectrum of Gas	as required			
IX. SHUTDOWN CONDENSER Shellside	62-23-003	pH	once/month	9.0 - 10.5	WC-1	250
	62-23-004					
		Chromate (ppm)	once/month	300 - 400	WC-10	50
		Phosphate (ppm)	once/month	25 - 30	WC-14	50
		Dissolved Solids (ppm)	once/month		WC-5	1000
		Suspended Solids (ppm)	once/month		WC-6	See Method
		Total Solids (ppm)	once/month	1000	WC-7	100
X. FEEDWATER	65-23-001	pH	3 times/wk	7.0 ± 0.5	WC-1	250
	65-23-002					
		Conductivity (μmhos-cm)	3 times/wk	1.0	WC-2	250
		Chloride (ppm)	3 times/wk	0.1 max	WC-3	25
		Copper (ppm)	once/wk		WC-12	50
		Iron (ppm)	once/wk		WC-4	50
		Silica (ppm)	once/wk	0.1	WC-16	50
		Dissolved Oxygen (ppm)	once/wk	0.02 ± 0.02	WC-8A	See Method (Check after changing demin.)
		Dissolved Solids (ppm)	once/wk		WC-5	1000
		Suspended Solids (ppm)	once/wk		WC-6	See Method
		Total Solids (ppm)	once/wk		WC-7	100
		Gross β-γ Activity (μc/cc	once/month		RC-14	
		Gross Alpha Acticity (μc/cc)	once/month		RC-3	
		Gamma-ray Spectrum of Water	once/month			
XI. MAIN STEAM	64-23-001					
Condensed Steam	64-23-002	Chloride (ppm)	once/month	0.1 max	WC-3	25
		Conductivity (μmhos-cm)	once/month	1.0 max	WC-2	250
		Dissolved Oxygen (ppm)	once/month		WC-8A	See Method

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number	Sample Aliquote (ml)
Condensed Steam (Cont'd)		Silica (ppm)	once/month	0.1 max	WC-16	50
		Copper (ppm)	once/month		WC-12	50
		Gamma-ray Spectrum of Water	once/month			
XII. FULL FLOW CONDENSATE DEMIN.						
From Hot Well Condensate Pump	63-23-001	pH	daily	7.0 ± 0.5	WC-1	250
		Conductivity (μmhos-cm)	daily	1.0 max	WC-2	250
		Chloride (ppm)	daily	0.1 max	WC-3	25
		Copper (ppm)	once/wk		WC-12	50
		Iron (ppm)	once/wk		WC-4	50
		Silica (ppm)	once/wk		WC-16	50
		Dissolved Oxygen (ppm)	once/wk	0.02 ± 0.02	WC-8A	See Method Value expected is .005 - .01 ppm
		Gross Alpha Activity (dpm-ml)	once/month		RC-3	
		Gross β-γ Activity (dpm-ml)	once/month		RC-14	
		Gamma-ray Spectrum of Water	once/month			
		Dissolved Solids (ppm)	once/month		WC-5	1000
		Suspended Solids (ppm)	once/month		WC-6	See Method
		Total Solids (ppm)	once/month		WC-7	100
Service Tank Sampling	63-23-002	pH		7.0 ± 0.5	WC-1	250
	63-23-003	Conductivity (μmhos-cm)	as required	1.0 max	WC-2	250
	63-23-004	Chloride (ppm)	as required	0.1 max	WC-3	25
		Copper (ppm)	as required		WC-12	50
		Iron (ppm)	as required		WC-4	50
		Silica (ppm)	as required		WC-16	50
		Dissolved Oxygen (ppm)	as required		WC-8A	See Method
		Gross Alpha Activity (dpm-ml)	as required		RC-3	
		Gross β-γ Activity (dpm-ml)	as required		RC-14	
		Gamma-ray Spectrum of Water	as required			
		Dissolved Solids (ppm)	as required		WC-5	1000
		Suspended Solids (ppm)	as required		WC-6	See Method
		Total Solids (ppm)	as required		WC-7	100
Cation Regeneration	63-25-003	pH	as required	7.0 ± 0.5	WC-1	250
Anion Regeneration	63-25-034	Conductivity (μmhos-cm)	as required	1.0 max	WC-2	250
		Suspended Solids (ppm)	as required		WC-6	See Method
		Dissolved Solids (ppm)	as required		WC-5	1000
		Total Solids (ppm)	as required		WC-7	100
		Gross β-γ Activity (dpm-gm)	as required		RC-14	

System Description	Sample Valve Number	Analysis	Frequency	Limits	Method Number	Sample Aliquote (ml)
Anion Regeneration (Cont'd)		Gamma-ray Spectrum of Resin	as required			
Caustic Tank Inlet Sample	63-23-009	pH	as required		WC-1	250
		Conductivity	as required		WC-2	250
XIII. DEMINERALIZED MAKEUP AND WELL WATER		pH	once/wk		WC-1	250
		Conductivity (μ mhos-cm)	once/wk		WC-2	250
		Chloride (ppm)	once/wk		WC-3	25
		Silica (ppm)	once/month		WC-16	50
		Copper (ppm)	once/month		WC-12	50
		Iron (ppm)	once/month		WC-4	50
		Gross β-γ Activity (uc/cc)	once/month		RC-14	
		Total Solids (ppm)	once/month		WC-7	100

APPENDIX A

SPECTROPHOTOMETRIC ANALYSIS

PRINCIPLE

Introduction

In order to provide a logical basis for measurement of the absorption of light, it is necessary to allow for losses by reflection and by scattering at the boundaries of the cell that contains the medium and also for the small losses caused by scattering within the medium itself. This correction is made by comparing the intensity I of the ray of light that has passed through the absorption cell that contains the sample with the intensity I_0 of the ray of light after it has passed through a medium of similar refractive index contained in an identical cell. The ratio I/I_0 x 100 is then the percent transmittancy of the sample.

The absorption spectrum of a given medium can be expressed in the form of a graph of absorbancy versus wavelength. The shape of such a curve is more or less characteristic of the absorbing substance; however, the characteristics of the absorption spectrum also depend on several other factors, such as the thickness of the cell, the concentration of the absorbing substance, if the medium is a solution, and the chemical nature of the solvent and of the solute. Some media will give smooth absorption curves without well-marked points of inflection; this property is termed "general absorption". Other curves will show maxima or minima; this

APPENDIX A

SPECTROPHOTOMETRIC ANALYSIS

Introduction (Cont'd)

property, which is more common, is termed "selective absorption". All substances exhibit absorption in some region of the electromagnetic spectrum. For example, benzene shows a complicated group of maxima and minima in the ultraviolet region, whereas water shows strong absorption in the near infrared. These extensive invisible regions of the spectrum can be investigated spectrophotometrically and are more significant in some field of analytical chemistry than the visible region itself.

Treatment of Data

The analytical chemist is concerned primarily with spectrophotometric data insofar as it will aid him in the identification of an unknown substance, or in carrying out a quantitative determination of a constituent.

For the purposes of identification, a spectrum is obtained by plotting absorbancy measurements versus the wavelength in millimicrons at different wavelength settings. The curve is then compared with the absorption spectra of known substances. Identification is established when the absorption spectrum of the unknown can be superimposed on a known spectrum.

APPENDIX A

SPECTROPHOTOMETRIC ANALYSIS

Treatment of Data (Cont'd)

Quantitative determinations are preceded by the establishment of a calibration curve that is prepared by plotting absorbency (or extinction) as the ordinate versus the concentration of the substance as the abscissa on rectilinear graph paper. The wavelength setting chosen for the standard curve is usually the wavelength of maximum absorption. The absorbancy of the unknown is then measured and the concentration is determined by reference to the standard calibration curve. A separate calibration curve is established for each spectrophotometer.

OPERATING INSTRUCTIONS FOR DU-SPECTROPHOTOMETER

OPERATING CONTROLS - POWER SUPPLY

A. Power Switch

This two-position rotary switch turns the power supply on and off. The ON position supplies power, through the multi-conductor cable, to the electronic circuitry of the spectrophotometer and also supplies power, through the terminals on the output and of the power supply, to the tungsten lamp.

NOTE: Before turning Power Switch ON always turn the Filament Temperature Switch OFF. After turning the Power Switch ON, wait for one minute before turning the Filament Temperature Switch from the OFF position.

B. Filament Temperature Switch

This eight-position rotary switch, used in conjunction with the Source Circuit Switch, controls operation of a hydrogen lamp or mercury lamp by determining its filament and anode voltages. The OFF position removes all voltage from the socket. This position is used when the spectrophotometer is operated without either the hydrogen lamp or the mercury lamp.

C. Source Circuit Switch

This two-position switch used in conjunction with the Filament Temperature Switch, sets the anode voltage at the correct value for the hydrogen or mercury lamp.

OPERATING CONTROLS - POWER SUPPLY (Cont'd)

D. Photomultiplier Gain Switch

This eleven-position rotary switch, functional only if the spectrophotometer is operated with the photomultiplier tube, adjusts the sensitivity of the multiplier phototube by changing the voltage applied to the dynodes.

In addition to an OFF position, the switch has ten operating positions. The Full position provides maximum sensitivity. Clockwise rotation of the switch decreases the sensitivity. This switch is used as a coarse sensitivity adjustment for the sensitivity knob on the DU.

E. Zero Suppression Switch

This six-position rotary switch applies a bucking voltage to compensate for background radiation effects in flame, fluorescence, or reflectance measurements.

F. Screen Bias Switch

This five-position rotary switch controls the screen-bias voltage on the 2532 tube in the amplifier circuit of the spectrophotometer.

Ordinarily, adjustment is required only infrequently, and then as a result of tube aging or replacement. This switch is a coarse adjustment for the dark current control on the DU.

OPERATING CONTROLS - POWER SUPPLY (Cont'd)

G. Operation with Tungsten Lamp

To operate the spectrophotometer with the tungsten lamp use the following procedure:

1. Turn DU Shutter Switch OFF.
2. Turn DU Tungsten Lamp Switch ON.
3. Turn DU Function Switch to CHECK position.
4. Turn power supply Power Switch ON.
5. Allow power supply to warm-up for about one hour.
6. Rotate the Wavelength Selector to set the desired wavelength.
7. Push Phototube Positioning Knob in to select the red-sensitive phototube (above 625 mu) or pull out to select the blue-sensitive phototube.
8. Make sure the load resistor is in position number 1.
9. Select proper filter if one is required.
10. Insert standard and sample cells, in the cell holder and place holder in the cell compartment. Replace compartment cover.
11. Use Sample Positioning Knob to position the standard cell in the light path.
12. Rotate Dark Current Control to zero meter needle.
13. Turn Shutter Switch ON.
14. Rotate Slit Adjustment Control to approximately zero the meter needle, or to set the desired slit width.
15. Rotate the Sensitivity Control to accurately zero the meter needle.
16. Turn Shutter Switch OFF.

OPERATING CONTROLS - POWER SUPPLY (Cont'd)

17. Use Sample Positioning Knob to position the unknown sample cell in the light beam.

18. Set Selector Switch to 1, or to 0.1 if the transmittance is less than 10 percent.

19. Turn Shutter Switch ON.

20. Rotate Transmittance Control to zero the meter needle.

21. Record the transmittance or absorbance reading.

22. Turn Shutter Switch OFF.

23. Use the Sample Positioning Knob to move the next unknown sample into the light beam, and repeat Step 12 and Steps 18 through 21, or repeat the proceeding measurement procedures with the sample at new wavelength or slit openings.

DESCRIPTION OF OPERATING CONTROLS - DU

A. Absorption Cells and Holder

The front position in the cell holder should be used for the cell that contains the reference liquid. The cells should be marked so that they can always be used in the same position in the cell holder. The cells should be compared by filling them with demineralized water. Before use, the cells should be cleaned with distilled water or other suitable solvent. Do not use hot concentrated acids which might etch the polished surfaces. Remove the cells from the holder for cleaning and filling. Make sure the cells are seated properly in the cell compartment and with the knob pushed in, replace the cover. Each cell can be moved into the light beam by pulling the slide knob to the appropriate stop.

DESCRIPTION OF OPERATING CONTROLS - DU (Cont'd)

B. Phototube Selection

The spectral range to be investigated determines the proper phototube to be used. The red-sensitive phototube is used above 624 mu and is in position when the knob is pushed IN. The bluc-sensitive phototube is used below 624 mu and is in position when the knob is pulled OUT as far as possible.

C. Filter Slide

The filter slide is located between the exit slit and the cell compartment and is operated by means of a knob on the front end. The front position knob pushed in, is blank and is used in the range 400 to 1000 mu and also with the hydrogen lamp. The second position contains a red-purple filter and is used in the range 400 to 320 mu with the tungsten lamp. The third position is blank and may be fitted with special filters if needed.

D. Sensitivity Control

For best performance, it is recommended that the sensitivity knob be used one to three turns from its clockwise limit. The most accurate readings on the Transmittance Scale can be obtained with the sensitivity knob set between the clockwise limit and the midpoint. The accuracy is within 0.1 percent at the clockwise limit. Maximum photometric resolution is attained when the Sensitivity Control is rotated

DESCRIPTION OF OPERATING CONTROLS - DU (Cont'd)

to its counterclockwise limit, since less light is required to zero the meter needle at 100 percent transmittance, permitting narrower slit widths to be used.

E. Wavelength Selector

This control adjusts the position of the quartz prism inside the monochromator and simultaneously rotates the calibrated Wavelength Scale. It is recommended that the wavelength settings be approached from the long wavelength end of the scale each time.

F. Tungsten Lamp Switch

This is a toggle switch located on the exterior of the lamp housing back plate.

G. Selector Switch

This is the main instrument switch and controls the function of the DU. The OFF position disconnects power to the DU. The check position provides a rapid means of adjusting the DU at 100 percent transmittance without having to turn the Transmittance Control. When the switch is in the 1 position the Transmittance Scale reads 0 to 110 percent transmittance, and the Absorbance Scale reads infinity to 0. Setting the Selector Switch at 0.1 position expands the Transmittance Scale for making measurements on samples having less than 11 percent transmittance.

DESCRIPTION OF OPERATING CONTROLS - DU (Cont'd)

H. Shutter Switch

Passage of light from the cell compartment to the phototube is controlled by the Shutter Switch on the phototube housing. This switch must be OFF to adjust dark current. When the switch is in the ON position, light transmitted through the sample reaches the phototube. Turn the switch gently from one position to the other.

I. Dark Current Control

Dark current is the current passing through the phototube and other circuit components when the phototube is not exposed to light. For accuracy of measurement, dark current must be balanced out of the circuit before each meter reading. The adjustment is made by turning the Shutter Switch OFF and bringing the meter needle to zero by rotating the Dark Current Control.

J. Phototube Load Resistor Switch

In the number 1 position, a 2000-megohm load resistor is equipped to be used with the tungsten, hydrogen, or mercury lamps. The "2" and "3" positions are reserved for special load resistors for special applications.

K. Null Meter

This meter indicates electrical balance of the instrument during various measurement procedures; i.e., dark current

DESCRIPTION OF OPERATING CONTROLS - DU (Cont'd)

adjustment, setting of the 100 percent reference point, etc.

L. Slit Adjustment Control

This rotary control adjusts the width of the curved bilateral entrance and exit slits simultaneously. The slits are continuously adjustable from .01 to 2 millimeters. Slit width settings are indicated on an accurately calibrated scale and should always be approached from the narrow width direction.

M. Transmittance Control

The transmittance control is used to balance the null meter at zero before reading the transmittance or absorbance of the sample. Positioning of the Selector Switch and the Sensitivity Control affects the sensitivity of the instrument and the readings of the calibrated Transmittance or Absorbance Scales.

APPENDIX B

USE AND CARE OF POLYETHYLENE

PROPERTIES

Polyethylene absorbs water extremely slowly. It has been found that the weight gained due to absorbed water is about 0.15% after a sample of polyethylene had been allowed to stand in water at room temperature for one year.

Polyethylene is relatively unreactive chemically. Concentrated caustic materials, such as ammonium hydroxide, potassium hydroxide, and sodium hydroxide, do not effect polyethylene. Potassium permanganate and hydrogen peroxide, at room temperature, does not attack it. Diluted acids, bases, and salt solutions show no corrosive action on it.

The temperature should be kept below 70 degrees C. Concentrated HNO_3, carbon disulfide, bromine, acetone, ether, toluene, ethyl acetate, lubricating oil, and turpentine should not be stored in polyethylene containers.

CARE

Ordinary soap and water can be used to clean the surface.

APPENDIX C

This method is to check the concentration of C-7 Silica Standard solution method WC-16 gravimetrically.

PROCEDURE

1. Pipet 5 ml from the method WC-16 silica standard solution into 150 ml beaker.

2. Add 5 ml of concentrated hydrochloric acid.

3. Evaporate the sample to dryness on a water bath with periodic additions of the three -5 ml portions of concentrated hydrochloric acid.

4. Dry the evaporated residue in an oven at 110°C for 1 hour.

5. Add 5 ml of concentrated hydrochloric acid and then add 50 ml of water to the dried residue in the beaker.

6. Warm the beaker and contents and stir to dissolve or suspend all the residue. Filter the warm solution through an ashless, medium filter paper.

7. Wash the residue on the filter paper 15 times with (1-49) hydrochloric acid and then several portions of water.

CAUTION: Cover the funnel containing the filter paper and its residue with a clean watch glass, and reserve it for later ignition.

APPENDIX C

PROCEDURE (Cont'd)

8. Return the filtrate to the original evaporating beaker and evaporate to dryness on a water bath with periodic addition of two 5 ml portions of concentrated hydrochloric acid.

9. Dry and repeat the filtration and washing steps 2 through 7 using a second funnel and filter paper.

10. Place both filter papers with its dehydrated residue in a tared porcelain crucible and dry under a heat lamp.

11. Cover and ignite for 10 minutes in a muffle furnace at 1000 to 1200°C.

12. Remove the cover and continue the ignition for 30 minutes.

13. Cool in a desiccator and weigh the crucible and precipitate on an analytical balance to the nearest 0.1 mg.

14. Repeat steps 12 and 13 until a constant weight is obtained.

15. Add several drops of concentrated sulfuric acid (H_2SO_4) and 5 ml of hydrofluoric acid (HF) to the weighed residue in the crucible and evaporate to dryness on a low-temperature hot plate.

16. Re-ignite the residue by repeating steps 12, 13 and 14.

APPENDIX C

CALCULATIONS

Calculate the concentrations of silica, in ppm as follows:

$$SiO_2, \text{ ppm} = \frac{(W_1 - W_2)\ (1000)}{V}$$

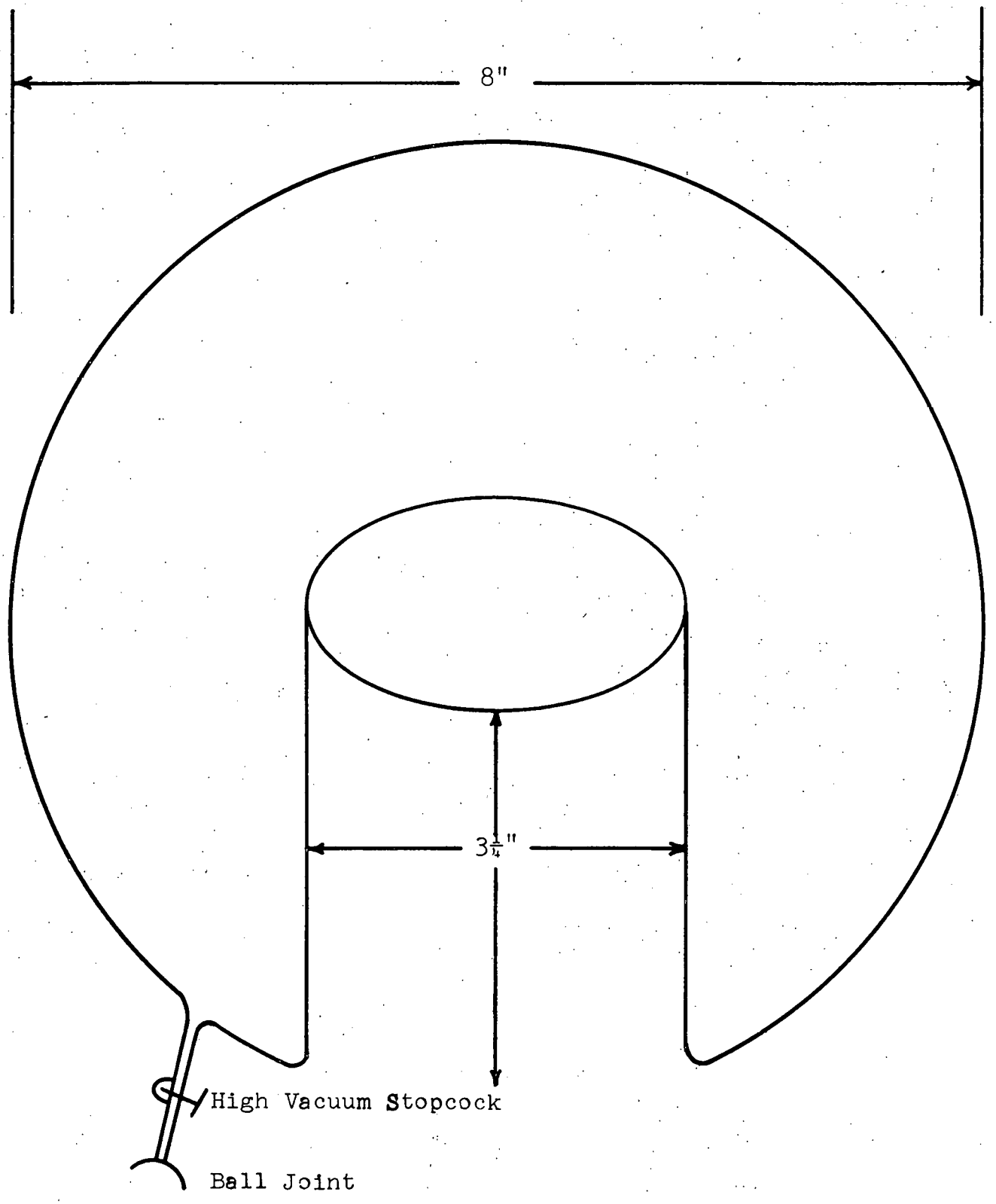
where:

W_1 - weight of crucible and sample residue, in milligrams after first ignition (step 14).

W_2 = weight of crucible and sample residue, in milligrams after treatment with HF and re-ignition (step 16).

V = milliliters of sample used from WC-16 method.

APPENDIX D



RADIOACTIVE GAS COUNTING CHAMBER

APPENDIX E

The following are the references for Sections IV and V Radio and Water Chemistry Methods:

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